LOW-SEVERITY COAL LIQUEFACTION
A CHALLENGE TO COAL STRUCTURE DEPENDENCY

ENEO C. MORONI

U.S. Department of Energy, FE-34 GTN, Washington, D.C. 20545 U.S.A.

INTRODUCTION

The purpose of this paper is to summarize recent information from coal
liquefaction studies in bench scale as well as in integrated process develop-
ment units, together with the data from new analytical techniques which have
provided substantial amounts of new information on several important aspects
of coal structure and coal reactivity. The results of these studies reveal
that existing coal models and current empirical tests for coal reactivity no
longer reflect adequately the new knowledge of coal structure and coal
reactivity.

Earlier approaches to direct coal liquefaction employed high-severity
operating conditions of pressure, temperature and coal/solvent slurry contact
time, to achieve in one reactor the highest coal conversion and distillate
yield possible. High-severity thermal processing did not necessarily lead
to reactions that were all desirable, but resulted in undesirable regression
reactions, such as polymerization, condensation and an increase in the aromatic
nature of the initially-formed coal fragments. Although elevated temperatures
may be necessary for the breakdown of the original coal structure, preventive
means, such as a kinetically rapid hydrogen transfer from a hydrogen donor
solvent to stabilize the overall solvent-coal adduct, have been employed to
mitigate the regressive reactions. However, because of lack of sufficient
transferable hydrogen to maximize the conversion of the asphaltols and
asphaltenes, which contain highly reactive functional groups, polymerization/
condensation and dealkylation reactions still occur, as evidenced by high
hydrocarbon gas yield.

DISCUSSION

The key role of the functional groups, and in particular of the phenols,
in promoting and participating in polymerization/condensation reactions is
well established (1). But the seemingly important function of the aliphatic
groups attached to the aromatic structure of the coal and of the donor
solvent is that of forming free radicals at high thermal severity,
competing kinetically and taking away the available hydrogen directed to
the condensed aromatic structure, which eventually goes to coke or insoluble
organic matter. The fate of the aliphatic groups in coals and those formed
by cracking hydrogenated aromatic rings during upgrading of the coal extracts,
has not been sufficiently studied, particularly in relation to their key
role in coal liquefaction. High thermal severity coal liquefaction processes,
which have monopolized bench scale research and scale-up efforts from the
early German discoveries to the present time, seem to have a pronounced
dependency on coal structure somewhat similar to those of coal gasification
and combustion, since all of these are operating above the activation energies
of all the major reactions involved and are dominated by an unordered

retrogressive condensation, cracking and transalkylation array of reactions. For these and other reasons the organic structure of coal has appeared to researchers as a highly crosslinked, amorphous and unreactive macro-molecular structure.

A more recent approach uses low-severity coal liquefaction in separated but integrated stages in order to optimize the coal dissolution and coal extract upgrading steps (2). This emerging technology and the development of new analytical techniques have produced results which change substantially our approach to coal liquefaction techniques, have inspired new thoughts in unraveling the complex mechanism of direct coal liquefaction at low-severity and more importantly give us a radically different picture of the structure and reactivity of coals than has been provided by high-severity liquefaction, gasification and combustion processes.

Important new information from this new approach includes:

o   Low-severity processing forms mostly reactive low molecular-weight fragments. If not properly quenched, these reactive fragments, which are formed in the very early stages of liquefaction, can condense to form structures similar to those produced by high-severity liquefaction (3).

o   Thermally produced coal extracts contain high levels of heteroatom compounds and are "refractory" to catalytic hydrogenation. Conversely low-severity produced extracts are low in heteroatoms and more easily hydrogenatable, and consistently yield excellent equilibrium hydrogen donor solvent (4).

o   Perhaps because of the occurrence of low molecular-weight reactive coal fragments, surrounded by a recycle solvent which is low in heteroatoms and rich in hydroaromatics, this approach appears to be successful in processing both high- and low-reactivity coals, and producing similar conversions and similar product qualities from both types of coal, supporting the notion that conversion and product quality is less dependent on coal characteristics and more dependent on process operation than previously believed (4).

o   Proton NMR analysis, modified to provide data on distillate and non-distillate fractions, served to create a working kinetic model for coal extract hydroprocessing, thus enabling us to distinguish catalytic hydrogenation from ring opening and particularly from dealkylation of the highly alkylated condensed hydroaomatic compounds produced by low-severity liquefaction, and to predict solvent donor quality as well as the yield structure of the upgraded products (5).

Other important information has been obtained by various sources working at low-severity process conditions, but this information is mostly related to operability advantages, since processing was the main objective of the projects involved. Nevertheless, the limited information given here appears to disclose a completely different picture of the relationship between the structure and reactivity of coals and low-severity coal liquefaction.

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We are discovering more similarities in coal-derived products even though there are large differences in the structure of the coals from which these products are derived. These similarities become more evident as the coal/solvent donor slurry is processed at controlled low-severity in the extraction as well as in the upgrading steps under the conditions where equilibrium is more closely reached and in the presence of an aged catalyst with steady-state activity.

It is extremely difficult to capture in research bench scale units the essence of the results produced in an integrated continuous process because the rapid initial deactivation of fresh catalyst provides continuously changing conditions leading to rather confusing results. Also, most of the key data and benefits, i.e., increased coal conversion, enhanced donor quality, and increased formation of few major condensed hydroaromatic compounds, are obtained only after several cycles of the integrated continuous staged operation. At process equilibrium, benzopyrenes, phenanthrenes and chrysenes and their highly alkylated derivatives constitute more than 60 percent of the total product, whether a bituminous or a subbituminous coal is employed as the starting material (6).

R&D COORDINATION

Current research efforts on coal liquefaction are leading to further improvement in the understanding of the mechanism of reactions occurring at even lower temperatures and overall less severe processing conditions, revealing that coal, asphaltols and asphaltenes are much more reactive species than previously thought. It can be stated that there is a turn of events occurring in direct coal liquefaction, which from a steady evolutionary progress, has recently become a revolutionary processing approach. Preliminary results indicate that this approach will provide a much larger "equalizer" effect on processing any type of coal, making it even more process dependent rather than coal type dependent (7).

On the basis of the above new information, evidently there is an urgent need for in-depth discussion between researchers who are dedicated to unravelling coal characteristics, mechanisms and reactivities and those who are devoted to coal processing and the kinetic aspects of the reactions involved in each phase of the low-severity coal liquefaction process.

Due to changing economics, the introduction of new large-scale coal conversion processes has been postponed and, as a consequence, more time is available for research to gain fundamental insights into coal structure and to obtain a better understanding of its impact on coal liquefaction.

Therefore, the recent exciting results obtained in the development of an emerging technology in direct coal liquefaction should be discussed, possibly in small-scale symposia, as a supplement to the large-scale conferences, i.e., ACS, AIChE, Contractors' and Coal Science Conferences and thus provide the opportunity for in-depth discussions and a maximum profit from exchange of knowledge and ideas, and better utilization of research talents and dollars.

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A Critical Temperature Window for Coal Hydropyrolysis

Martin L. Gorbaty and Peter S. Maa

Exxon Research and Engineering Company
Annandale, NJ 08801

Abstract

Pyrolysis of coals in the presence of hydrogen is known to enhance liquid yields, but this enhancement is often accompanied by increases in methane make. In many instances increased methane yields are detrimental because of the amount of hydrogen consumed to make methane. This paper will discuss the discovery of a critical temperature threshold for coal hydropyrolysis, below which little methane is formed, and above which significant methane is produced. A simple procedure is described to determine the critical temperature, which is different for each coal and pressure regime used.

INTRODUCTION

Coal has an atomic hydrogen to carbon ratio less than unity. To make desirable liquids, with atomic H/C ratios of 1.5 to 2, hydrogen must be added or carbon removed. The latter approach involves pyrolysis of the coal to produce liquids, gases and a carbonaceous residue called coke or char depending on whether the coal became plastic during the pyrolysis. In the past many researchers have tried to increase the yield of liquids by performing the pyrolysis in the presence of hydrogen under pressure[1-6]. In general, these researchers obtained increased liquid and hydrocarbon gas (C_1 to C_3) yields from such hydropyrolysis methods relative to pyrolysis under inert atmospheres. These increases came at the expense of significant hydrogen uptake, and the hydrogen reported mainly to the hydrocarbon gases.

In our studies of coal hydropyrolysis, we confirmed the yield increase trends previously observed. While examining the effect of temperature on the hydropyrolysis reaction we found that a temperature threshold exists, below which increased liquid yields are obtained without production of large quantities of hydrocarbon gases. Details of this finding are described in this paper.

EXPERIMENTAL

Hydropyrolysis reactions were carried out in a fixed bed apparatus, a schematic diagram of which is shown in Figure 1. The 620 cc reactor was capable of sustaining pressures of up to 13.3 MPa, and was heated by means of a fluidized sand bath, which could be raised and lowered hydraulically. In a typical experiment, about 400g of coal was charged into the hopper above the reactor and pressurized with either nitrogen or hydrogen. The reactor was placed in the fluidized sand bath and heated at a rate of about 4°C/min, with preheated nitrogen or hydrogen flowing through it at a rate of about 0.4 SCFM at a predetermined reaction pressure. At an appropriate temperature, coal from the hopper was charged to the reactor by opening a butterfly valve, while the heating rate was adjusted to about 2°C/min. Volatile products were carried out of the reactor by the flowing gas into a high pressure knock out vessel. After reducing gas pressure to 1 atm it was passed through a cooled low pressure knockout vessel then into a wet test meter. Gas samples were taken every 10 minutes and analyzed on a Carle GC. At the end of the experiment, the sand bath was lowered, the reactor cooled, and liquid and char products were collected. Figure 2 shows typical temperature profiles for both the sand bath and reactor during constant temperature coal pyrolysis under nitrogen. Reactor

temperature drops as coal is added, but rapidly recovers to the temperature of the sand bath.

Determination of the critical temperature threshold was accomplished by following the above procedure using hydrogen gas at a flow rate of 0.4 SCFM. Coals were addded to the reactor at a temperature of 360°C and heating was continued to 525°C. In Figure 3 the temperatures of the sand bath and the reactor are plotted for a typical experiment. We define the critical temperature as the point where the exotherm begins.

RESULTS AND DISCUSSION

Pyrolysis under hydrogen is known to produce higher yields of liquid and hydrocarbon gas products relative to pyrolysis under nitrogen. This was verified using a subbituminous coal following the above procedure, at a pressure of 7MPa and a constant temperature of 525°C. In the hydrogen case, an exotherm was noted after 3 minutes. Figure 4 shows the evolution of gases on a cumulative basis from the coal during pyrolysis under nitrogen at 525°C, and Figure 5 shows cumulative gas evolution and hydrogen consumption rate for the reaction under 7 MPa of hydrogen at 525°C. In the nitrogen case, liquid yield was 10 wt% (dry coal basis), while under hydrogen, liquid yield was 14 wt%. Notably different were the methane yields in nitrogen and hydrogen, 2 wt% for the former and almost 15 wt% for the latter. From Figure 5 it can be seen that hydrogen consumption rate parallels methane evolution, which implies that the increased methane yield is due to the some form of hydro-gasification of the coal or char.

To better understand this observation, the hydropyrolysis was carried out under the programmed temperature conditions described above. Figure 3 shows the temperature profile. Clearly an exotherm occurs at about 45 minutes residence time (temperature of about 465°C). Figure 6 shows the gas evolution for this reaction from which it can be seen that significant methane evolution occurs at about the same time as the exotherm. We define the temperature at which the exotherm appears as a critical temperature threshold.

As indicated in Table 1, the critical temperature threshold appears to be dependent upon hydrogen pressure, decreasing with increasing pressure. Once again the yield of oil is relatively constant, but the methane make is directly related to hydrogen pressure.

Table 1

Onset of Exotherm and Methane Yield Related to Hydrogen Pressure

(370-525°C; 0.4 SCFM)

HYDROGEN PRESSURE, MPa	1.4	7.0	9.2
EXOTHERM, °C	488	465	437
YIELDS, WT% COAL			
METHANE	7.0	11.9	23.0
$C_2 + C_3$	2.2	2.4	2.2
OILS	12.8	14.7	14.8
CHAR	55.3	44.6	38.0
HYDROGEN CONSUMPTION (wt% coal)	2.32	3.76	5.14

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The effect of the exotherm on product yields and hydrogen consumption was determined by carrying out the hydropyrolysis in such a way that the reaction temperature never exceeded the critical temperature, which for this coal at these reaction conditions was 465°C. Figure 7 displays the thermal history of this experiment. Several minutes before the critical temperature was reached, the sand bath was lowered, thus assuring that the maximum temperature did not exceed the critical temperature. It is apparent from the figure that the exotherm was completely eliminated in this experiment. Figure 8 shows the gas evolution with time, and it can be seen that methane make is low and in the same range as that for pyrolysis under nitrogen. Table 2 shows a direct comparison of the yield patterns from the hydropyrolysis conducted below and above the critical temperature.

Table 2

Higher Temperature Increases Conversion to Gas Not Oil.

(0.4 SCFM; 7MPa H_2)

YIELDS (WT% COAL)	372-465°C 35 MIN	371-525°C 85 MIN
METHANE	1.4	11.2
$C_2 + C_3$	1.2	2.4
OILS	14.3	14.7
CHAR	64.5	44.6
HYDROGEN CONSUMPTION (wt% coal)	0.6	3.7

It is obvious from these data that higher pyrolysis temperatures do increase overall conversions, but it is striking that oil yields change very little. Most of the conversion increase is manifested in the methane make. The most significant finding from these data is that hydrogen consumption increases six fold at the higher temperature without adding to the liquid yield. The additional hydrogen appears to be consumed in producing methane.

All of the data discussed to this point was taken on a subbituminous coal. To determine whether the effect is important for coals of different rank, the hydropyrolysis was carried out on a bituminous coal. The data for these experiments are summarized in Table 3 and compared to those from the subbituminous coal. In these experiments the bituminous coal was impregnated with a concentrated potassium hydroxide solution to aid in preventing agglomeration. The treated coal contained 8.44 wt% acid soluble potassium. The critical temperature for this coal was determined in separate experiments to be 474°C and the hydropyrolysis was carried out below the temperature. It can be seen from Table 3 that liquid yield from the bituminous coal increased by about twofold under these hydropyrolysis conditions, while the hydrocarbon gas make is only slightly higher than that produced under nitrogen. Much more work on other coals must be done before a firm conclusion can be made regarding generality, but the data gathered thus far support this as a tentative conclusion.

Virtually nothing is known with certainty regarding the mechanism or mechanisms involved in this phenomenon. One obvious mechanism for methane formation is hydrodealkylation of side chains. If dealkylation is a major pathway, it should be possible to observe differences in the infrared spectra of hydropyrolysis chars made above and below the critical temperature. Figure 9a is a Fourier Transform IR

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Table 3

Critical Temperature Threshold May be General

	SUBBITUMINOUS	BITUMINOUS*
CRITICAL TEMP., °C	465	474
LIQUID YIELD (WT% DAF) IN		
H_2	15.5	18.7
N_2 (525°C)	11.3	9.7
C_1-C_3 (WT% DAF) IN		
H_2	2.8	6.4
N_2 (525°C)	5.6	5.0
CHAR (WT% DAF) IN		
H_2	61.5	58.4
N_2 (525°C)	66.4	68.1

* KOH treated

spectrum of the char from the hydropyrolysis reaction which produced 11.2 wt% methane (Table 2), and Figure 9b is the difference spectrum between Figure 9a and that of the spectrum of the char from the hydropyrolysis reaction which made 1.4 wt% methane (Table 2). Figure 9b does not indicate significant differences between the two chars. This appears to be inconsistent with a hydrodealkylation hypothesis.

Elemental analyses of the chars show that oxygen remaining in the chars decrease as more methane is made. These data are displayed in Figure 10, as methane yield plotted against atomic O/C ratio, and may indicate that carbon-oxygen bonds are the sites most readily attacked by hydrogen.

One set of mechanisms which appear to be consistent with the observations discussed above are those proposed by Graber and Hüttinger[7]. They subjected many aromatic, alkylaromatic and heteroatom-containing aromatic model compounds to hydro-pyrolysis at temperatures varying between 600-1000°C. Among their conclusions, they found that oxygen in aromatic rings and hydroxyl groups of phenol and naphthol strongly enhance the methane yield, and that decarbonylation was a key step for both types of oxygen compounds:
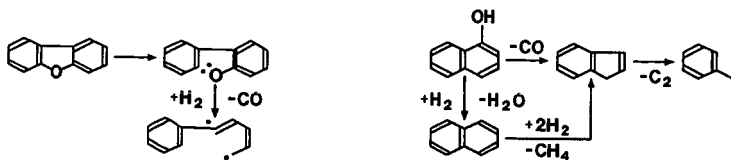
Nitrogen containing aromatic systems also showed a propensity to form methane under their conditions. Analyses of the chars described above showed an inverse dependence of methane yield to the atomic N/C ratio.

CONCLUSIONS

A critical temperature threshold exists for coal hydropyrolysis, above which methane forms rapidly with a concomitant increase in hydrogen consumption. Liquid yields are not increased above the critical temperature. The critical temperature threshold may be a general phenomenon, and depends upon coal, i.e., bituminous or subbituminous coal, hydrogen partial pressure and hydrogen treat rate. The chemistry and mechanisms involved in the effect are not well understood. Preliminary results indicate that dealkylation may not be a major route to methane formation, and that the reactions to produce methane take place at heteroatom sites, particularly oxygen and nitrogen, in the char.

This work suggests that controlling the temperature of the hydropyrolysis below that of the critical temperature is an important means to improve the utilization of hydrogen, thus improving the efficiency of any hydropyrolysis process.

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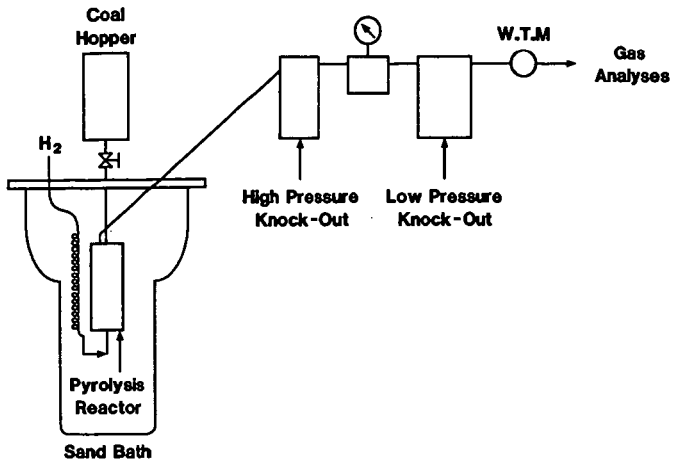
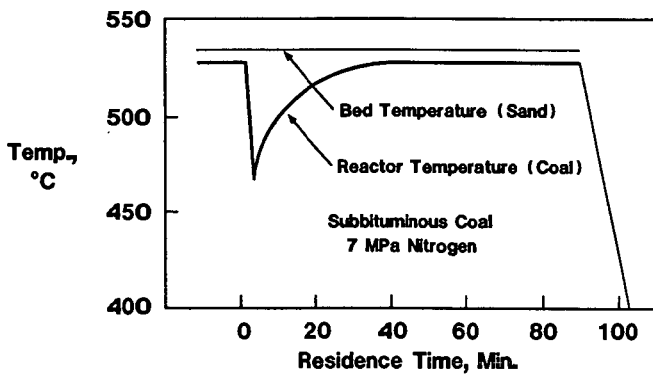Fig. 1. Fixed Bed Hydropyrolysis Apparatus

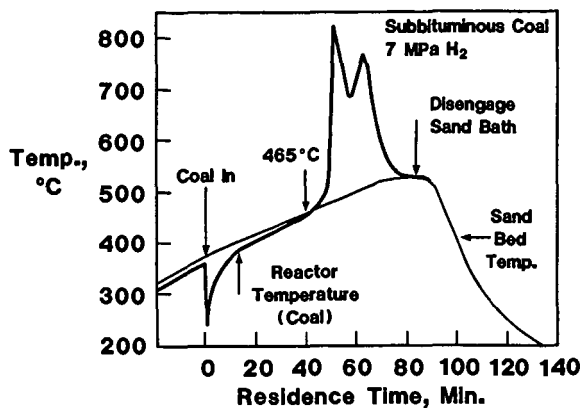Fig. 2. Typical Thermal History of Coal Under Nitrogen

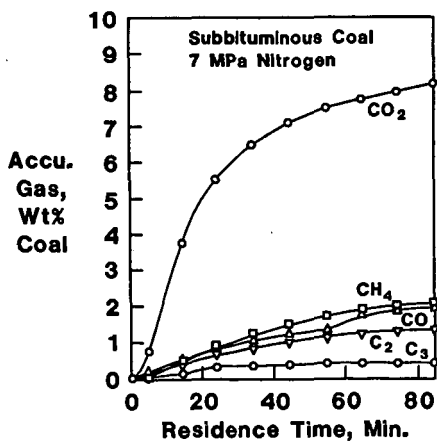Fig. 3. Programmed Hydropyrolysis Heatup Exhibits Exotherm

Fig. 4. Low CH_4 Yield From Nitrogen Pyrolysis at 525°C
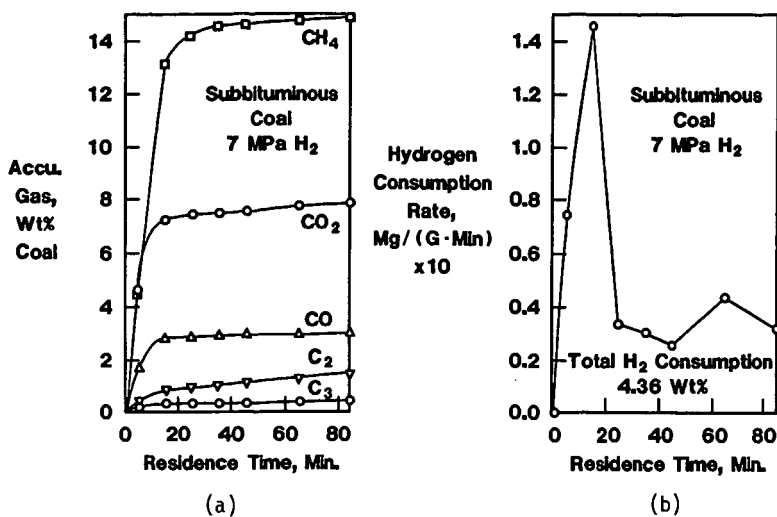
Fig. 5. (a) Gas Make and (b) Hydrogen Consumption Rate for Hydropyrolysis at 525°C
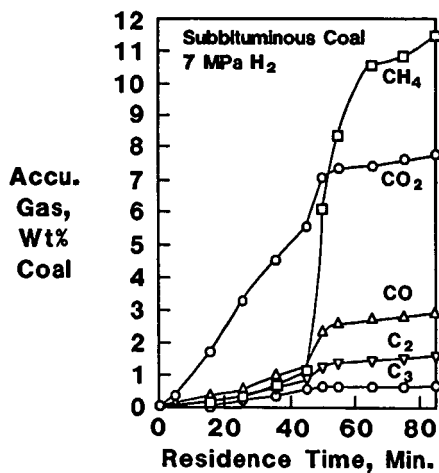
Fig. 6. Increased CH$_4$ Evolution with Onset of Exotherm
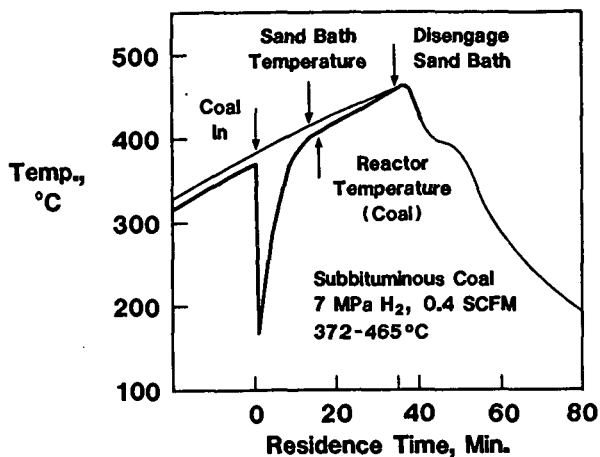
Fig. 7. Controlled Heatup to Below 465°C Eliminates Exotherm

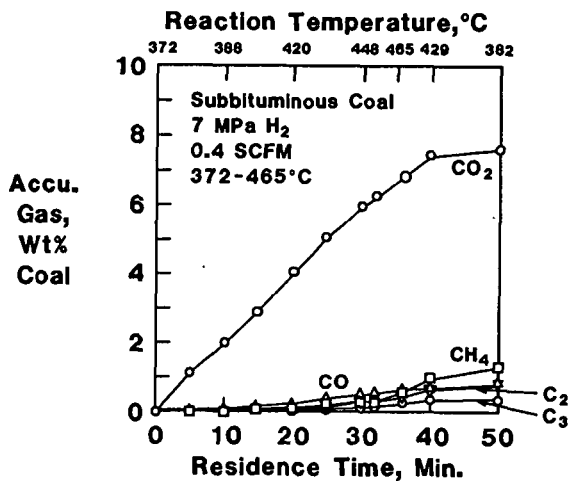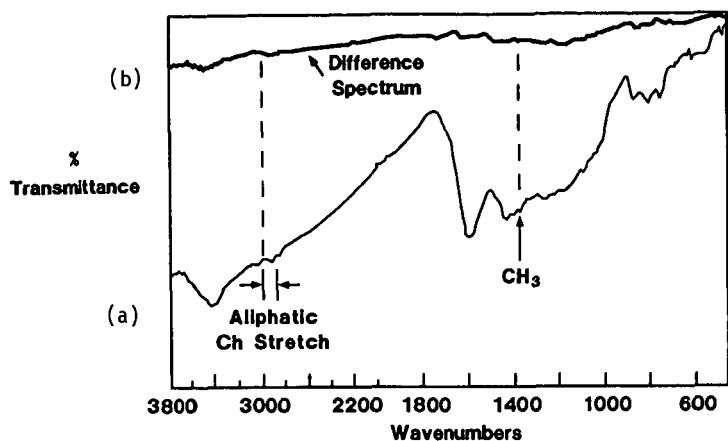

Fig. 8. Rapid Methane Formation is Eliminated

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Fig. 9. (a) FTIR Spectrum of Char (11.2 wt.% CH_4); (b) Difference Spectrum of Chars (11.2 wt.% CH_4 and 1.4 wt.% CH_4)
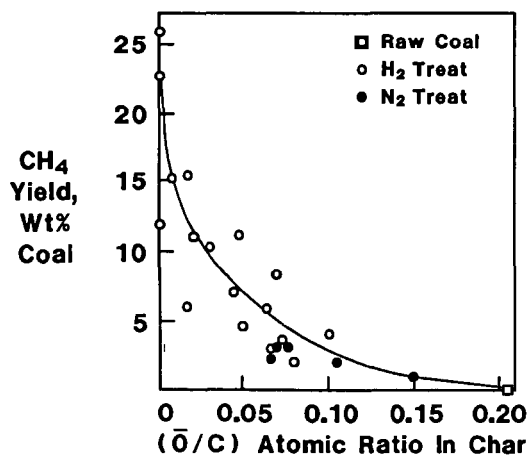

Fig. 10. Methane Yields Inversely Proportional to Oxygen in Char

LOW-TEMPERATURE COAL DEPOLYMERIZATION. 5. CONVERSION OF NEW MEXICO AND UTAH HVB COALS TO HYDROCARBON OILS

J. Shabtai*, T. Skulthai, and I. Saito**
Department of Fuels Engineering, University of Utah
Salt Lake City, Utah 84112

INTRODUCTION

The development of various low-temperature coal solubilization procedures, based on the application of selective chemical-catalytic reactions, has been reviewed in 1981 by Wender et al. (1)   Such procedures have recently attracted considerable interest in view of the obvious advantages of coal liquefaction under mild, subsoftening conditions. In the preceding paper of these series, we outlined a new approach to low-temperature coal depolymerization and liquefaction which involves the application of three consecutive reaction steps in which different types of intercluster linkages are subjected to preferential cleavage (2).   The procedure, as summarized in Figure 1, consists of the following sequential steps: (1) intercalation of the coal sample with catalytic amounts (3-15%) of $FeCl_3$ followed by mild hydrotreatment (HT) of the coal-$FeCl_3$ intercalate; (2) base-catalyzed depolymerization (BCD) of the product from step 1, under super-critical conditions; and (3) hydroprocessing (HPR) of the depolymerized product from the two preceding steps, using a sulfided CoMo catalyst. The high efficiency of the overall procedure was demonstrated by the previously reported conversion of a Wyodak coal sample into a light hydrocarbon oil product, containing 57.2 wt% (or 53.8 wt% calculated on the starting MAF coal) of low-boiling fractions (gasoline, kerosene and light gas oil; b.p. up to 305°C/760 torr).   The present paper provides additional examples of the application of the same procedure, using two higher rank coal samples from New Mexico and Utah.

EXPERIMENTAL

Materials. Two HVB coal samples, one from Fruitland, San Juan basin (New Mexico) referred below as F(NM) coal, and another from the vicinity of Helper (Utah) referred below as H(UT) coal, were provided by Amoco Oil Co. The ultimate analysis of the F(NM) coal sample (MAF basis) in wt% was C, 78.69; H, 6.00; N, 1.62; Cl, 0.07; S, 0.96; O (diff.), 12.66; H/C = 0.909; ash content (dry basis), 11.37; BTU/lb (dry basis), 12,691. The ultimate analysis of the H(UT) coal sample in wt% was C, 81.10; H, 5.97; N, 1.09; Cl, 0.03; S, 0.49; O (diff.), 11.32; H/C = 0.877; ash content (dry basis) 9.91%; BTU/lb (dry basis), 13,111.

The coal samples were grinded and sieved through a 200-mesh standard sieve in a nitrogen-purged glove box, and then stored under nitrogen in a refrigerator.

Catalysts. The catalyst used in the mild HT step of the depolymerization procedure (Figure 1) consisted of $FeCl_3$, which was intercalated in the powdered coal feed using a newly developed procedure (see below). The catalyst-solvent system, used in the subsequent BCD step consisted of a 10% alcoholic alkali hydroxide solution, preferably a methanolic KOH solution (2). In the final HPR step the catalyst used was sulfided 6Co8Mo/γ-Al_2O_3 prepared by incipient wetness impregnation of Ketjen γ-Al_2O_3 with an ammoniacal solution of ammonium paramolybdate, followed by impregnation with an aqueous $Co(NO_3)_2$ solution. This high Co content catalyst was

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* To whom correspondence should be addressed

**National Research Institute for Pollution and Resources, Yatabe, Tsukuba,
  Ibaraki, 305 Japan

found to be markedly more active for hydrodeoxygenation of depolymerized coal products and other oxygen-rich synfuels in comparison with conventional $3Co8Mo/\gamma-Al_2O_3$ catalysts (3).

Apparatus and Experimental Procedure. Mild Hydrotreatment (HT) Step. Each of the powdered coal samples was first pre-extracted with THF in a Soxhlet for 48 hr, yielding small amounts of solubles, including resins (7.6% from the F(NM) coal, and 9.2% from the H(UT) coal). The pre-extracted coal was then intercalated with catalytic amounts (3-15% by wt) of reagent grade $FeCl_3$, using the following procedure:

About 20 g of the pre-extracted coal was accurately weighed and placed together with the desired amount of $FeCl_3$ into a 100 ml glass tube, connected to a previously described impregnation apparatus (4). About 20 ml of acetone was then added to the tube and the coal-$FeCl_3$-acetone mixture was stirred in an ultrasonic bath at room temperature for 1 hr. The excess acetone was distilled off under a stream of nitrogen and the resulting $FeCl_3$-coal intercalate was transferred to a porcelain dish and dried overnight in a vacuum desiccator oven at 60°C/0.02 torr.

3-4 g portions of the dry intercalate were hydrotreated in a specially designed autoclave system described elsewhere (2). Conditions used were: temperature, 250-270°C; hydrogen pressure, 1000-1500 psig; reaction time, 1-2 hr. In all runs the experimental procedure was the same as previously employed in the mild hydrotreatment (HT) of a Wyodak coal sample (2). The hydrotreated product was transferred to a Soxhlet and back-extracted with acetone to remove the $FeCl_3$ catalyst. Recovery of the latter was essentially quantitative (>99.5%) due to the low hydrotreatment temperature. The extracted product was subsequently extracted also with THF to recover a small amount (usually <10% by wt) of soluble products from the above HT step.

Base-Catalyzed Depolymerization (BCD) Step. The hydrotreated, $FeCl_3$-free coal product from the above HT step, in admixture with the above-mentioned small amount (<10% by wt) of solvent-free THF-soluble material, was subjected to BCD in a 150 ml autoclave, using a 10% methanolic KOH solution as depolymerizing agent. In all runs the amount of the hydrotreated coal feed was between 3-4 g, and the KOH solution/coal weight ratio was 10:1. The weighed coal sample and KOH solution were charged to the autoclave, and the latter was purged and then pressurized with nitrogen to an initial pressure of 1,000 psig. The autoclave was quickly heated (15°C/min) to the desired temperature in the range of 250-290°C, at which point stirring at 500 rpm was started and continued for 1 hr. With completion of the run the autoclave was quickly cooled down with water and depressurized. The product was transferred to a beaker and acidified with aqueous 2N HCl solution to pH = 2. The water-insoluble organic material was separated, thoroughly washed with distilled water, and finally dried in a desiccator at 100°C/0.2 torr. The dry product was then extracted with THF in a Soxhlet for 24 hr, leaving a solid residue consisting mainly of the original coal ash. In some experiments the solvent-free BCD product was fractionated into cyclohexane-solubles (oils), benzene-solubles, cyclohexane-insolubles (asphaltenes), and residual THF-solubles, benzene-insolubles (asphaltols), using a sequential procedure in which the total THF soluble, solvent-free BCD product was first extracted with benzene, and the resulting benzene-soluble fraction was freed from the solvent and then extracted with cyclohexane to separate it into oil and asphaltene fractions.

Hydroprocessing (HPR) Step. The total product from the sequential HT-BCD depolymerization steps (or in some experiments the oil fraction of the product) was subjected to hydroprocessing with a sulfided $6Co8Mo/\gamma-Al_2O_3$ catalyst (see above), using a 300 ml stirred autoclave and mesitylene as a solvent.

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In each run about 5 g of the depolymerized coal product was dissolved in 50 ml of mesitylene and charged together with 1 g of catalyst and several drops of CS_2 to the autoclave. The latter was purged with nitrogen, pressurized with hydrogen to an initial pressure of about 1500-1700 psig, quickly heated (15°C/min) to the selected reaction temperature (350-370°C), and then additionally pressurized with hydrogen to a reaction pressure of 2700 psig. The autoclave was stirred under these conditions for 4 hr, and then cooled down and depressurized. In some experiments the catalyst was exchanged at this point with a fresh catalyst portion (1 g) and the hydroprocessing repeated for another 4 hr. At the end of the run, the HPR product was quantitatively removed from the autoclave, separated by filtration from the catalyst, and analyzed.

Product Analysis. Depolymerized products from the sequential HT-BCD steps and the final hydrocarbon products from the HPR step were subjected to a combination of IR, C^{13} NMR, PMR and elemental analysis. The boiling point distribution of such products was determined by simulated distillation using a 18" x 0.25" stainless steel gas chromatographic column packed with 3% Dexsil 300 on Anakrom Q. A Hewlett-Packard, Model 5730 gas chromatograph was programmed for operation between -30° to 370°C at a rate of 11°/min (final temperature hold, 4 min; FID temperature, 400°C). Boiling point curves were calibrated with a standard mixture of C_0-C_{24} 1-phenylalkanes. GC data were fed directly, stored and calculated in a Hewlett-Packard 21MX E-series computer.

RESULTS AND DISCUSSION

Mild Hydrotreatment (HT) Step. Suitable conditions for mild hydrotreatment (HT) of the two $FeCl_3$-coal intercalates were first determined. This included determination of the optimal concentration of intercalated $FeCl_3$, the HT temperature, and the reaction time under which there is only partial breakdown of the coal framework by preferential cleavage of alkylene (e.g., methylene), benzyletheric, and some activated aryletheric intercluster linkages, with minimal (usually <10%) attendant solubilization (2,4).

Figure 2 shows the change in the yield of THF-solubles from mild HT (at 250°C) of the $FeCl_3$-F(NM) and $FeCl_3$-H(UT) coal intercalates as a function of $FeCl_3$ concentration. As seen, for the F(NM) coal $FeCl_3$ concentrations in the range of 8-12.5% by wt are sufficient for an HT step characterized by a desired, low-extent of solubilization (<10%). The slightly higher rank H(UT) coal, however, shows quite different behavior, as expressed in relatively much higher yields (ca 16-20%) at low $FeCl_3$ concentrations (5-10%) and markedly decreased yields of THF-solubles at higher $FeCl_3$ concentrations (15-20%). Figure 3 shows, however, that the yield of THF-solubles from HT of the $FeCl_3$-H(UT) coal intercalate can be brought down to the desired level (<10%) by decreasing the hydrotreatment time to about 1 hr (at 250°C). It is also seen in Figure 3 that increase in HT temperature to 290°C causes an excessive extent of solubilization which is undesirable from the point of view of the efficiency of the overall sequential depolymerization procedure. Specifically, the optimal conditions for the HT step were previously defined as those under which the extent of depolymerization and solubilization in the subsequent BCD step are maximal (see below) (2). Data summarized in Figure 3 show that low concentrations of $FeCl_3$ (5-10%) in the H(UT) coal intercalate are preferable to a higher concentration of this halide for HT at 250°C and 1-2 hr reaction time. On the basis of these results for the H(UT) coal a $FeCl_3$ concentration of 5% by wt, a temperature of 250°C, and a reaction time of 1-2 hr were selected as operating conditions for the HT of H(UT) coal. Figures 2 and 4, on the other hand, indicate that for the F(NM) coal a suitable set of HT conditions is a $FeCl_3$ concentration of 8-12.5%, a temperature of 250°C, and a reaction time of 1-2 hr. After removal of the intercalated $FeCl_3$ catalyst at the end of the mild HT step (see Experimental), the mildly hydrotreated F(NM) and H(UT) coals were subjected to base-catalyzed

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depolymerization (BCD), and the total yields of THF-soluble, depolymerized coal products from the sequential HT-BCD procedure determined (see below, Table 1).

Base-Catalyzed Depolymerization (BCD) Step. Table 1 summarizes the total yields of THF-soluble, depolymerized products from BCD of mildly hydrotreated F(NM) coal as a function of the temperature used in the preceding HT step. As seen, increase in HT temperature from 250° to 290°C results in gradual decrease in the yield of THF-solubles obtained in the BCD step (from 89.6% by wt for an HT temperature of 250°C to 68.0% for a temperature of 290°C). It is further seen that application of BCD alone to the same coal, without HT as preceding step (expt. 60) yields a markedly lower yield of THF-solubles (48.8%) as compared with that obtained by the combined HT-BCD procedure (compare with expt. 66 or 63), under otherwise identical BCD conditions. In experiment 66 the solubilization of the F(NM) coal is complete, as the insoluble residue left after the BCD step consists of the original coal ash only. Fractionation of the total THF-soluble product from the sequential HT-BCD processing shows that it consists mostly (>60% by wt) of cyclohexane-soluble (oil) components. In a series of comparative experiments, the conditions in the HT step were kept constant and identical with those in experiment 66, but the BCD step was performed at three different temperatures, i.e., 275°, 290° and 320°C. Fractionation of the products using solubility differences (see Experimental) showed that the oil fraction increases with increase in BCD temperature and becomes predominant at 290-320°C while the concentration of the combined asphaltene and asphaltol fractions reaches very low levels (<20% by wt). This behavior is consistent with previously reported results on the effect of BCD temperature upon the depolymerization of a Wyodak coal sample (2). It is also consistent with some earlier results which have shown that the product from base-catalyzed depolymerization of a Clear Creek, Utah coal at 320°C with NaOH-ethanol as depolymerizing agent consists predominantly of monocluster components(5).

Table 2 shows the change in the yield of THF-soluble products from BCD of mildly hydrotreated H(UT) coal as a function of BCD temperature in the range of 250-290°C, using otherwise identical conditions in both the HT and BCD steps. As seen, the total yield of THF-solubles increases with increase in BCD temperature from 37.0% (or 41.1% on the MAF coal) at 250°C to 72.6% (or 80.6% on the MAF coal) at 290°C. Complete solubilization of the H(UT) coal at 290°C requires extension of the BCD time to about 2 hr. It is also seen that BCD at 290°C without preliminary mild hydrotreatment (HT) of the coal (expt. 73) results in much lower solubilization yield (45.7%) as compared with that obtained by sequential HT-BCD (72.6%), using an identical temperature in the BCD step (expt. 74). Furthermore, the product from expt. 74 consists primarily (>60%) of cyclohexane-soluble (oil) components whereas the product from expt. 73 (without HT) contains only 21.8% of such components.

Hydroprocessing (HPR) of Depolymerized F(NM) and H(UT) Coals. Table 3 summarizes the elemental compositions of F(NM) and H(UT) depolymerized coal samples, as well as of products obtained from them in the last, i.e., the hydroprocessing (HPR) step of the sequential liquefaction procedure (Figure 1). As seen, the depolymerized coal samples retain the oxygen present in the starting coals, viz., the depolymerizing HT and BCD steps do not cause any appreciable extent of hydrodeoxygenation. However, structural studies based on C^{13} NMR, PMR and FTIR analysis of the products show that there is a major change in the oxygen functionality of the depolymerized coals as compared with the starting coals, i.e., most aryletheric and some dibenzofuranic intercluster linking groups undergo hydrolytic cleavage during the BCD step to yield phenolic groups (6). It is also seen in Table 3 that HPR of the depolymerized coals results in exhaustive hydrodeoxygenation, yielding hydrocarbon products of very low oxygen content. Structural analysis of HPR products and parallel model compound studies have elucidated the nature of some of the main depolymerizing reactions occurring in the HPR step, i.e., hydrogenolytic cleavage of condensed furanic rings (dibenzofuranic groups) and of Ar-Ar bonds (3,6). The reactions of such strong

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Table 1

Yield of THF-Soluble Products from BCD of Mildly Hydrotreated
F(NM) Coal as a Function of Temperature in the HT Step

Experiment, no.	60	66	63	61	62
HT step[a]					
Temperature, °C	--	250	250	275	290
$FeCl_3$ concentration	--	8.0	12.5	12.5	12.5
Yield of THF Solubles in HT Step, % by wt	--	6.0	6.7	8.6	14.8
BCD step[b]					
Temperature, °C	275	275	275	275	275
Total yield of THF-solubles, % by wt[c]	48.8	89.6	84.5	75.2	68.0
Insoluble residue[d]	51.2	10.4	15.5	24.8	32.0

[a]Initial H_2 pressure, 1500 psig; reaction time, 2 hr. [b]Initial N_2 pressure, 1000 psig; reaction time, 1 hr. [c]Total yield of depolymerized, THF-soluble products from sequential HT-BCD. [d]Including ash and non-depolymerized coal.

Table 2

Yield of THF-Soluble Products from BCD of Mildly Hydrotreated
H(UT) Coal as a Function of the Temperature in the BCD Step

Experiment no.	71	72	74	73
HT step[a]				
Temperature, °C	250	250	250	--
$FeCl_3$ concentration, % by wt	5	5	5	--
Yield of THF-Solubles in the HT Step, % by wt	12.9	12.5	12.4	--
BCD step[b]				
Temperature, °C	250	275	290	290
Total yield of THF-Solubles. % by wt[c]	37.0	59.4	72.6	45.7
Insoluble residue[d]	63.0	40.6	27.4	54.3

[a-d]See corresponding footnotes a-d, Table 1.

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Table 3

Elemental Composition of Depolymerized F(NM) and H(UT) Coals
and of Hydrocarbon Products Derived from them in the HPR Step

Element, % by wt.	Depolymerized coal[a]		Hydroprocessed (HPR) product[b]	
	F(NM)	H(UT)	F(NM)	H(UT)
Carbon	77.71	77.35	88.38	88.97
Hydrogen	8.34	8.74	10.04	9.83
Nitrogen	0.93	0.50	0.35	0.21
Sulfur	0.14	0.11	<0.01	<0.01
Oxygen (by difference)	12.88	13.29	1.23	0.99

[a]The depolymerized F(NM) coal sample was obtained by HT at 250°C,
followed by BCD at 275°C (see expt. 66, Table 1); the depolymerized
H(UT) coal sample was obtained by HT at 250°C followed by BCD at 290°C
(see expt. 74, Table 2).

[b]The hydroprocessing (HPR) of the depolymerized coals was performed at
370°C and 2700 psig H_2 pressure, using a sulfided 6Co8Mo catalyst and
mesitylene as a solvent (for procedure, see Experimental).

Table 4

Boiling Point Distribution of Depolymerized F(NM) and H(UT)
Coals and of Hydrocarbon Products Derived from them
by Hydroprocessing (HPR)[a]

Fraction (b.p., °C) wt %	Depolymerized coal[b]		Hydroprocessed (HPR)[c] product	
	F(NM)	H(UT)	F(NM)	H(UT)
Gasoline (<200°)	5.0	1.1	18.0	18.7
Kerosene (200-275°)	3.5	4.2	35.5	27.2
Gas Oil (275-325°)	11.1	5.1	8.1	9.4
Heavy Gas Oil (325-400°)	9.4	6.9	7.2	7.7
Vacuum Gas Oil (400-538°)	12.7	5.7	10.6	13.9
Total Distillable (<538°)	41.8	23.0	79.4	76.9
Atmospheric Residue (>350°)	75.6	87.0	36.3	42.2
Vacuum Residue (>538°C)	58.2	77.0	20.6	23.1

[a]Boiling point distributions were determined by simulated distillation
(see Experimental). [b]See footnote a, Table 3. [c]See footnote b, Table 3.

intercluster linkages involve as a first necessary step ring hydrogenation of at least one aromatic ring adjacent to the linkage, followed by C-O or C-C hydrogenolysis, respectively (3,6).
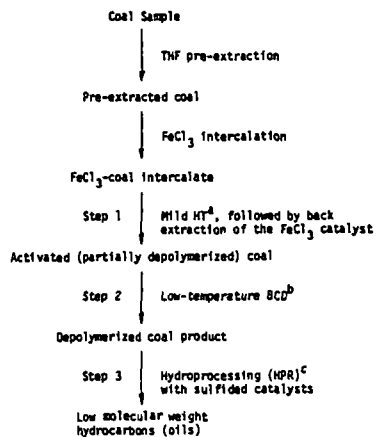
Table 4 summarizes the boiling point distribution of the depolymerized F(NM) and H(UT) coals, and of the hydrocarbon products derived from them in the HPR step. As seen, the oxygen-rich depolymerized coals are characterized by low volatility, as reflected in a total proportion of distillable components (<538°C) of 41.8% for the F(NM) coal and 23.0% for the H(UT) coal. The total proportion of gasoline- plus kerosene- range fractions is only 8.5% for the depolymerized F(NM) coal, and 5.3% for the depolymerized H(UT) coal. Hydroprocessing results in a dramatic change in volatility as reflected in a combined yield of 61.6% of low-boiling fractions (gasoline, kerosene, and gas oil; b.p. up to 325°C/760 torr) for the product from the F(NM) coal, and an yield of 55.3% of such fractions for the product from the H(UT) coal. Those results are similar to those previously reported for a lower rank Wyodak coal, and provide further support for the above outlined processing concept according to which preferential conversion of coals to light hydrocarbon oils requires in-depth, low-temperature coal depolymerization to monocluster products, prior to hydroprocessing.

ACKNOWLEDGMENTS

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Coal Sample

| THF pre-extraction

Pre-extracted coal

| FeCl$_3$ intercalation

FeCl$_3$-coal intercalate

Step 1 | Mild HT[a], followed by back
            extraction of the FeCl$_3$ catalyst

Activated (partially depolymerized) coal

Step 2 | Low-temperature BCD[b]

Depolymerized coal product

Step 3 | Hydroprocessing (HPR)[c]
            with sulfided catalysts

Low molecular weight
hydrocarbons (oils)

[a]HT = hydrotreatment (250-275°C; H$_2$ pressure, 1000-1500 psig)
[b]BCD = base-catalyzed depolymerization (250-285°C; initial N$_2$
       pressure, 1000 psig)
[c]HPR = hydroprocessing (350-370°C; H$_2$ pressure, 2700 psig)

Figure 1. Low-Temperature Coal Depolymerization-Liquefaction
          Procedure.

Figure 2. Yield of THF-Soluble Products from Mild HT of FeCl3-F(NM)
          Coal and FeCl3-H(UT) Coal Intercalates as a Function of
          FeCl$_3$ Concentration (250°C; 2 hr).

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Figure 3. Yield of THF-Soluble Products from Mild HT of FeCl$_3$-F(NM) Coal Intercalate as a Function of HT Temperature(°C) and Time (FeCl$_3$ Concentration, 12.5% by wt.)
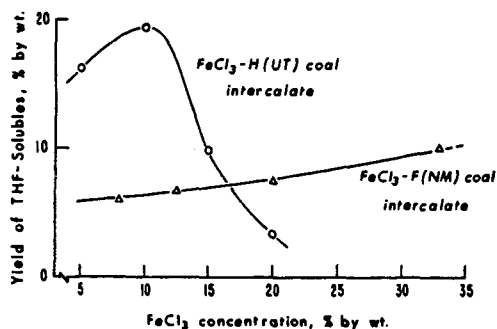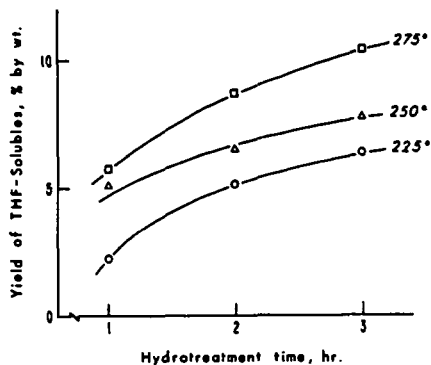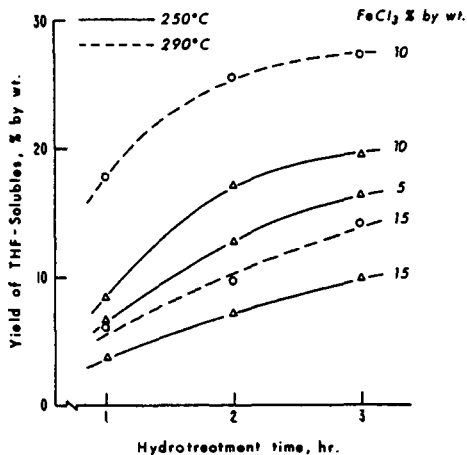

Figure 4. Yield of THF-Soluble Products from Mild HT of FeCl$_3$-H(UT) Coal Intercalate as a Function of FeCl$_3$ Concentration and Reaction Time.

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Thermal Effects on Liquefaction of Kentucky
#9 Coal with NiMo/AL$_2$O$_3$ Catalyst

K. C. Kwon

Chemical Engineering Department
Tuskegee University
Tuskegee, Alabama 36088

Introduction

The main objectives of this research are (1) to investigate effects of
heating rates on deactivation of catalysts, (2) to identify interactions
between hydrogen donor solvents (HDS) and catalysts, (3) to study effects
of initial temperatures on catalytic activities, and (4) to elucidate
interactions between physical solvents and catalytic activities in the
early stage of coal liquefaction.

A series of liquefaction experiments were conducted for Kentucky #9
coal (Ky #9 coal) without hydrogen donor solvents in the presence of
presulfided fresh Shell 324 M catalyst, increasing liquefaction tempera-
tures from 200°C or 300°C up to 380°C and holding liquefaction temperatures
at 380°C for 15 min (4,5). Naphthalene (NAP) was hydrogenated with
molecular hydrogen in the presence of used catalysts to evaluate catalytic
activities of used catalysts. Liquefaction of Ky #9 coal decreases and
catalytic activities increase, as heating rates increase, as shown in
Figure 1. The initial liquefaction temperatures appear to affect lique-
faction of Ky #9 coal in the presence of presulfided fresh Shell 324 M
catalyst, whereas catalytic activities appear to be independent of the
initial temperatures in the absence of hydrogen donor solvents.

When hexadecane (HEX) was used instead of 1-methylnaphthalene (1-MN)
as a physical solvent, both liquefaction of Ky #9 coal and deactivation of
Shell 324 M (NiMo) catalyst are less in the presence of Hex than 1-MN.

Another series of liquefaction runs of Ky #9 coal were performed in
the presence of both presulfided fresh Shell 324 M catalyst and various
hydrogen donor solvents such as anthracene (AN), 9,10-dihydroanthracene
(DHA), phenanthrene(PN), 9,10-dihydrophenanthrene(DHP), quinoline(Q), and
1,2,3,4-tetrahydroquinoline(THQ) (1, 2, 6, 7). The liquefaction tempera-
ture was increased from 200°C or 300°C up to 380°C in the heating rates
of 1-6°C/min.

Liquefaction of Ky #9 coal decreases, as heating rates increase, as
shown in Figures 3 through 6. The initial liquefaction temperatures appear
to affect both liquefaction of Ky #9 coal and deactivation of Shell 324 M
catalyst in the early stage of liquefying Ky #9 coal in the presence of
hydrogen donor solvents. Deactivation of Shell 324 M catalyst appears to
decrease with increasing heating rates. On the other hand, the initial
temperatures appear to affect liquefaction of Ky #9 coal and seem not to
affect deactivation of Shell 324 M catalyst in the absence of hydrogen
donor solvents.

Experimental

Coal liquefaction runs were conducted, using Ky #9 coal. Either
hexadecane or 1-MN was utilized as a physical solvent. A 13 cc, 316
stainless steel microreactor was fed with 1 g coal, 0.1 g hydrogen donor

solvent, 2.9 g physical solvent, 0.1 g presulfided fresh Shell 324 M
catalyst and 1200 psig hydrogen at room temperature, as shown in Table 1.
Q, THQ, AN, DHA, PN, and DHP were introduced in the reactor as hydrogen
donor solvents. Liquefaction temperatures were increased from 200°C or 300°
C up to 380°C and held at 380°C for 15 min.
        Following coal liquefaction at the desired reaction time and tempera-
ture, the reactor was quenched in cold water and the gaseous products were
released. The liquid-and-solid liquefaction products as well as the used
catalyst were removed completely from the reactor by dissolving these
liquefaction products with tetrahydrofuran(THF). The catalyst was
separated from the solid-and-liquid liquefaction products and then was
washed with 200 cc THF by sonicating the spent catalyst in THF for 12 min.
        The liquefaction products were separated into a THF soluble fraction,
a toluene-insoluble fraction and a cyclohexane-insoluble fraction to obtain
a product distribution in terms of preasphaltene(PRA), asphaltene(ASP) and
oil-plus-water-plus-gas (OWG) (8).
        Naphthalene was hydrogenated with molecular hydrogen in the presence
of the sonicated spent catalyst to examine deactivation of spent catalyst,
as shown in Table 2.
        Conversions of hydrogen donor solvents were analyzed, using a gas
chromatograph, equipped with a flame-ionization detector and an 8 ft. long,
1/8 inch OD, SP 2100 packed column.

Discussions

        A series of Ky #9 coal liquefaction runs were carried out without
hydrogen donor solvents, in the presence of presulfided fresh Shell 324
(NiMo) catalyst, increasing liquefaction temperatures from 200°C or 300°C
up to 380°C and holding liquefaction temperatures at 380°C for 15 min., as
shown in Figure 1.
        Coal liquefaction decreases with increasing heating rates and levels
off at high heating rates. Deactivation of catalyst also decreases with
increasing heating rates. The initial temperatures appear to affect lique-
faction of Ky #9 coal, whereas the initial temperatures do not appear to
affect deactivation of catalyst in the early stage of liquefying Ky #9 coal
in the absence of hydrogen donor solvents. Figure 1 shows that liquefac-
tion of Ky #9 coal in the absence of HDS significantly takes place at low
heating rates and does not take place at high heating rates between
liquefaction temperatures 200°C and 300°C. These data also suggest that
deactivation of catalyst in the absence of HDS does not appear to occur
significantly between liquefaction temperatures 200°C and 300°C.
        When hexadecane as a physical solvent was used instead of 1-MN, both
liquefaction of Ky #9 coal and deactivation of catalyst were lower in the
presence of hexadecane than 1-MN in liquefying Ky #9 coal in the absence
of hydrogen donor solvents, as shown in Figure 1. These facts may indicate
that both liquefaction of Ky #9 coal and deactivation of catalyst in the
absence of HDS are affected by physical solvents.
        Another series of coal liquefaction runs of Ky #9 coal were carried
out in the presence of both presulfided fresh Shell 324 M catalyst and
various hydrogen donor solvents such as AN, DHA, PN, DHP, Q, and THQ, using
1-MN as a physical solvent. The liquefaction temperature was increased
from 200°C or 300°C up to 380°C in the heating rates of 1-6°C/min, as shown
in Figures 2 through 6.
        Both liquefaction of Ky #9 coal and deactivation of catalyst decrease
with increasing heating rates. The initial temperatures affect both
liquefaction of Ky #9 coal and deactivation of catalyst in the presence of
HDS. These observations may explain that both liquefaction of Ky #9 coal
and deactivation of catalyst take place in the presence of HDS between

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liquefaction temperatures 200°C and 300°C.

Ky #9 coal was liquefied more in the presence of hydroaromatics such as DHA and DHP than corresponding aromatics such as AN and PN between liquefaction temperatures 200°C and 300°C, as shown in Figures 2, 3 and 6. These facts may elucidate that availability of donative hydrogen from hydrogen donor solvents is quite important in the early stage of liquefying Ky #9 coal in the presence of NiMo catalyst (3).

Deactivation of catalyst significantly takes place in the early stage of liquefying Ky #9 coal in the presence of HDS between liquefaction temperatures 200°C and 300°C, as shown in Figures 2 through 6, whereas deactivation of catalyst does not appear to take place in the early stage of liquefying Ky #9 coal in the absence of HDS between liquefaction temperatures 200°C and 300°C, as shown in Figure 1. These facts may indicate that hydrogen donor solvent itself appears to contribute to deactivation of catalyst in the early stage of liquefying Ky #9 coal.

Liquefaction of Ky #9 coal in the presence of Q decreases less with increasing heating rates than that in the presence of THQ. Deactivation of catalyst in the presence of Q decreases with increasing heating rates, whereas deactivation of catalyst in the presence of THQ decreases and then increases with increasing heating rates, as shown in Figures 4 and 5. This observation may suggest that THQ as a hydrogen donor solvent appears to poison catalyst at high heating rates in the early stage of liquefying Ky #9 coal.

Effects of various hydrogen donor solvents on liquefaction of Ky #9 coal were compared on a THF-solubles-vs-heating rates plot, as shown in Figure 6. The THF solubles-vs-heating rates curves for AN, DHA, Q and THQ are concave upward, whereas THF-soluble-vs-heating rates curves for PN and DHP are concave downward. Effects of heating rates on liquefaction of Ky #9 coal in the presence of quinoline appear to be least among others. These observations may indicate that characteristic plots of THF-solubles-vs-heating rates data are dependent on types of hydrogen donor solvents in the early stage of liquefying Ky #9 coal in the presence of Shell 324 M (NiMo) catalyst.

Conclusions

The following conclusions were made on the basis of the available data in this research.

- Initial temperatures appear to affect liquefaction of Ky #9 coal, whereas initial temperatures do not appear to affect deactivation of Shell 324 M (NiMo) catalyst in the early stage of liquefying Ky #9 coal in the absence of hydrogen donor solvents (See Figure 1)

- Physical solvent itself appears to affect both coal liquefaction and catalytic deactivation in the early stage of liquefying Ky #9 coal in the absence of HDS. (See Figure 1)

- Initial temperatures affect both coal liquefaction and catalytic deactivation in the early stage of liquefying Ky #9 coal in the presence of HDS. (See Figures 2 through 5)

- Hydrogen donor solvent itself appears to contribute to catalytic deactivation in the early stage of liquefying Ky #9 coal. (See Figures 1 vs Figures 2 through 5)

- Characteristic plots of THF-soluble-vs-heating-rate data are depen-

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dent on types of hydrogen donor solvents in the early stage of liquefying Ky #9 coal in the presence of Shell 324 M (NiMo) catalyst

. Quinoline behaves as a hydrogen donor solvent least sensitive to heating rates among others and THQ appears to poison catalyst at high heating rates in the early stage of liquefying Ky #9 coal in the presence of Shell 324 M (NiMo) catalyst and 1-MN as a physical solvent

. Coal liquefaction as well as catalytic deactivation can be identified, estimated and compared over a desired temperature range of coal liquefaction by liquefying coals at nonisothermal liquefaction temperatures

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Table 1

Liquefaction Conditions of Ky #9 Coal

Initial Temperatures (I.T.) (°C):   200 or 300

Final Temperature   (°C):   380

Heating Rate (°C/Min)   :   1-6

Liquefaction Duration
 at 380°C (Min)   :   0 or 15

Reactor Charge

  Hydrogen(H_2)   :   1200 psig at room temperature

  Coal   :   1 g

  Physical Solvent :   2.9 g or 3 g 1-Methylnaphthalene
                         or 3 g Hexadecane

  Hydrogen Donor
     Solvent   :   0.1 g

  Presulfided
  Fresh Shell
  324 M Catalyst   :   0.1 g

Table 2

Reaction Conditions of Evaluating Deactivation of Catalyst

   Reaction Temperature   :   380°C

   Reaction Duration   :   15 min.

   Reactor Charge

       Naphthalene   : 0.1 g

       Hydrogen   : 1200 psig at room temperature

       Used Catalyst   :   0.1 g

       Hexadecane   :   2.9 g

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Figure 1

Effects of Heating Rates on liquefaction of Ky #9 coal and deactivation of pre-sulfided fresh Shell 324 M catalyst in the absence of HDS, increasing liquefaction temperatures from 200°C or 300°C up to 380°C and holding liquefaction temperatures at 380°C for 15 min.

THF - Soluble (W %, MAF)

Initial Temp(°C) Physical Solvents
200°C   1-MN
300°C   1-MN
200°C   HEX

Conversion of Naphthalene (W %)

H₂: 1200 psig (cold)
Coal: 1 g
Physical Solvent: 3 g
Catalyst: 1 g

Heating Rates (°C/min)

Figure 2

Effects of Heating Rates on both lique-faction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M cata-lyst in the presence of AN, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.

THF - Soluble (W %, MAF)

Initial Temp (°C)
200
300

H₂: 1200 psig (cold)
Coal: 1 g
AN: 0.1 g
1-MN: 2.9 g
Catalyst: 0.1 g

Conversion of Naphthalene (W %)

Heating Rates (°C/min)

Figure 3

Conversion of Naphthalene (W %)

THF - Soluble (W %, MAF)

Heating Rates (°C/min)

H₂: 1200 psig (cold)
Coal: 1 g
DHA: 0.1 g
1-MN: 2.9 g
Catalyst: 0.1 g

Initial Temp(°C)
○ 200
□ 300

Figure 3

Effects of Heating rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of DHA, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.

Figure 4

Conversion of Naphthalene (W %)

THF - Soluble (W %, MAF)

Heating Rates (°C/min)

H₂: 1200 psig (cold)
Coal: 1 g
Q: 0.1 g
1-MN: 2.9 g
Catalyst: 0.1 g

Initial Temp(°C)
○ 200
□ 300
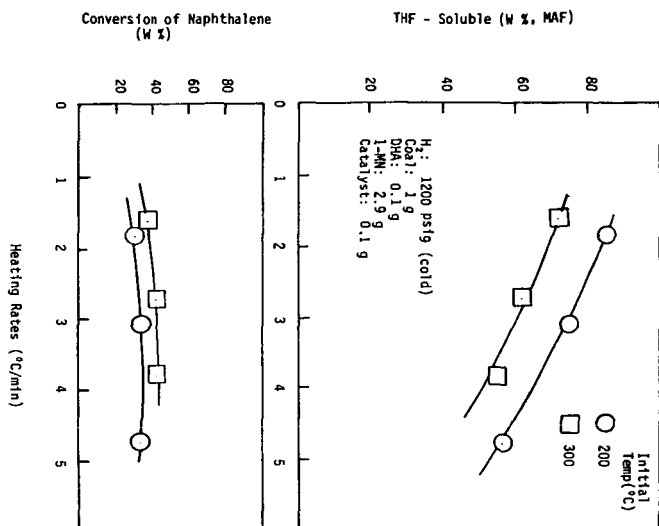
Figure 4

Effects of heating rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of Q, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.

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Conversion of Naphthalene (W %)

THF – Soluble (W %, MAF)

Heating Rates (°C/min)

○ 200
□ 300

Initial Temp (°C)

H₂: 1200 psig (cold)
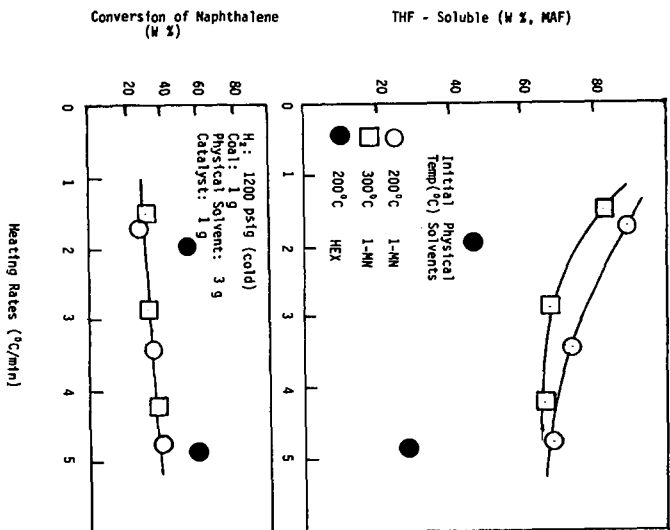Coal: 1 g
THQ: 0.1 g
1-MN: 2.9 g
Catalyst: 0.1 g
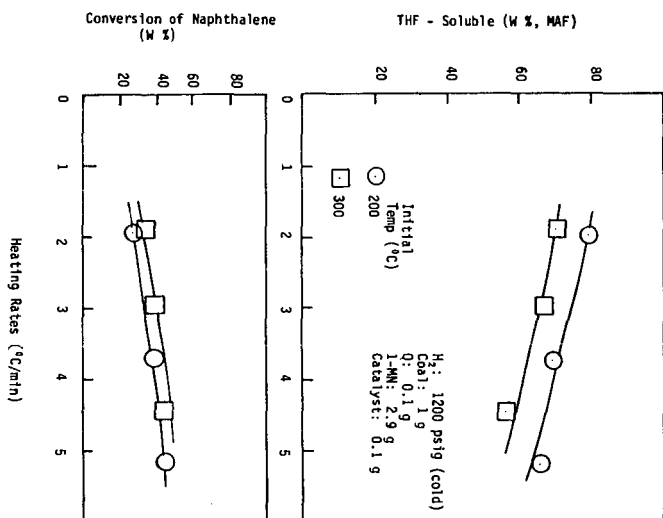
Figure 5

Effects of heating rates on both liquefaction of Ky #9 coal and deactivation of presulfided fresh Shell 324 M catalyst in the presence of THQ, increasing liquefaction temperatures from 200°C or 300°C up to 380°C.
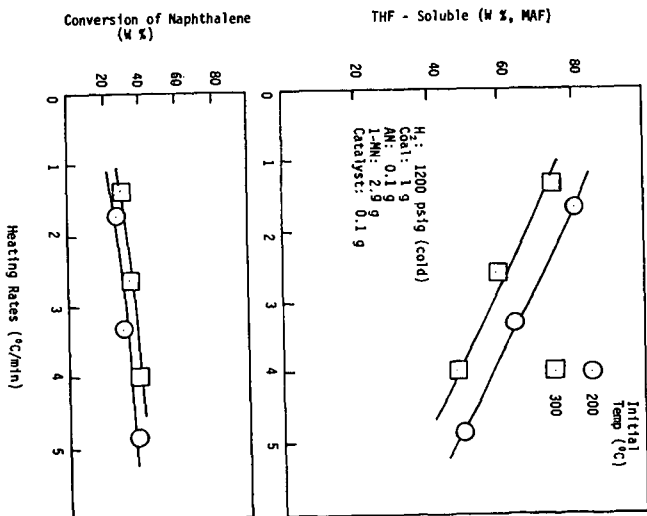
THF – Soluble (W %, MAF)

Heating Rates (°C/min)

THQ
Q
DHA
AN
DHP
PN
NONE

H₂: 1200 psig (cold)
Coal: 1 g
HDS: 0.1 g
1-MN: 2.9 g
Catalyst: 0.1 g

Figure 6

Effects of heating rates on liquefaction of Ky #9 coal in the presence of various HDS and presulfided fresh Shell 324 M catalyst, increasing liquefaction temperatures from 200°C up to 380°C.

MODERATE TEMPERATURE COAL HYDROGENATION

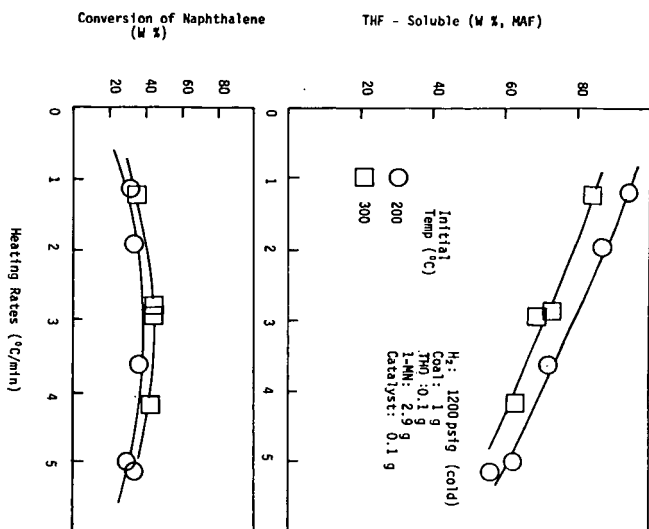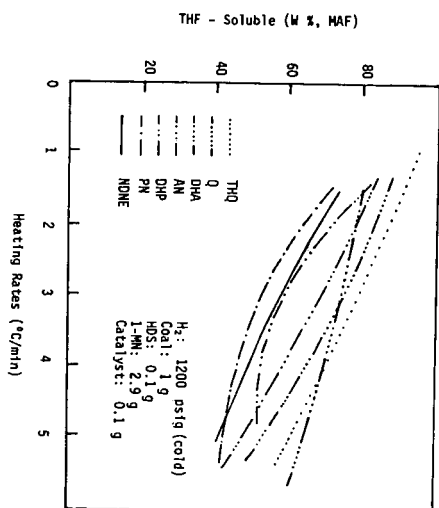Raymund P. Skowronski and Laszlo A. Heredy

Rockwell International, Rocketdyne Division
6633 Canoga Avenue, Canoga Park, CA, 91304, U.S.A.

INTRODUCTION

A well-defined correlation among coal structure, the reaction conditions of liquefaction, and the composition of the products is an important fundamental objective of coal liquefaction research. This objective has been very elusive because of the great complexity of the coal structure and because of the many side reactions that occur at commercial liquefaction temperatures. Such side reactions include thermal fragmentation, and the condensation or polymerization of reactive intermediates, which result in gas and coke formation.

Additional complications are caused by the use of a donor solvent in most coal liquefaction processes. The donor solvent interferes with the investigating of the reaction chemistry and analyzing of the reaction products by forming adducts with the coal-derived intermediates. Furthermore, it is difficult to characterize separately the donor solvent and its derivatives in the complex product mixture. At moderate reaction temperatures, internal hydrogen rearrangement may play a relatively more significant role in radical stabilization. Consequently, hydrogenating coal with gas-phase hydrogen and without a donor solvent offers significant advantages in understanding the mechanisms that occur.

The reaction of coal with H_2 has been investigated in the temperature range of 400 to 500°C (1). At these temperatures, however, cracking and condensation reactions that lead to gas and coke formation are fast and take place indiscriminately. The objective of this research was to explore hydrogenation at lower temperatures where the thermal side reactions are less extensive.

EXPERIMENTAL

The hydrogenation experiments were conducted in a 1-liter stirred autoclave equipped with a liner and a specifically designed anchor-type impeller. It is essential to use a properly designed impeller in this reaction to improve gas-solid contact and mass transfer, particularly during the initial softening of the coal particles, when caking can occur. A liner made of Inconel 600 and an impeller made of 316 SS were used in Experiments 1A through 1E and in Experiment 2. The liner and impeller were coated with glass for Experiments 3 and 4 to eliminate the catalytic effect of the metal surface. In each experiment, 25 g of high volatile bituminous coal was used. The coal was ground to -200 mesh and dried at 115°C in vacuo before use.

Two sets of hydrogenation experiments were conducted using two bituminous coals of slightly different rank. The objective of the first set was to investigate reactions in the 275 to 325°C range using 1-h and 48-h reaction times. The objective of the second set was to explore the effect of coal rank and two catalysts on coal conversion and product oil characteristics. Reaction parameters were selected on the basis of the results of the first set of experiments.

The first set was conducted using a Pittsburgh seam bituminous coal of the following composition (%, daf): C:80.1, H:5.1, S:3.6, N:1.6, and O:9.6. The dry coal contained 11.2% ash. The second set was conducted at 325°C using reaction times of 48 h. A Pittsburgh seam bituminous coal of somewhat higher rank was used in these experiments. The elemental composition of this coal (%, daf) was as follows: C:82.1, H:5.9, S:3.3, N:1.6, and O:7.1. The ash content of the dry coal was 8.2%.

Each experiment was conducted at a hydrogen pressure of approximately 20.7 MPa. After the product gases had been measured and analyzed, the hydrogenated product was Soxhlet-extracted with benzene. The benzene solution was concentrated by distillation and then poured into excess hexane to precipitate the asphaltenes. After filtration, the hexane solution was distilled and the hexane evaporated to recover the oil fraction. The benzene-insoluble residue was Soxhlet-extracted with THF and separated into a THF-soluble fraction and an insoluble residue. This procedure was based on a separation method recommended by Mima et al (2). The solvent-separated fractions were analyzed for elemental composition. A detailed characterization of the product oils was made using simulated distillation, vapor phase osmometry, field ionization mass spectrometry (FIMS), and proton nuclear magnetic resonance (NMR) spectrometry.

RESULTS AND DISCUSSION

The test conditions and product yields of the first set of experiments are presented in Table 1. Very little reaction was observed by visual inspection or chemical analysis in a 1-h reaction period at the lowest test temperature (275°C). The appearance of the dry powder product very closely resembled that of the starting coal. Most of the gas products consisted of carbon oxides; the gaseous hydrocarbon (CH_4) yield was only 0.04%. Compared with the starting coal, the amount of the THF-soluble extract increased from 5% to 8%. Some of these results have been presented elsewhere (3).

An experiment made using D_2 under the same conditions (1B), however, showed that a significant H-exchange had taken place at 275°C. About 15% of the protium (^1H) in the coal was replaced by deuterium (^2H or D). In this experiment, a sizable increase in the THF solubility also was observed. At 310 to 325°C, the product was a shiny black solid, and there were significant increases in the THF solubility. Finally, when the reaction time was increased to 48 h at 325°C, the THF solubility of the product increased to 77%. Of this amount, 72% was hexane-soluble oil (daf coal basis). The fraction of gaseous products increased only slightly as the temperature was increased from 275 to 325°C, and the reaction time increased from 1 h to 48 h. This indicates that the product liquids were stable under these experimental conditions. The structural characterization of the product oil from this last experiment at 325°C for 48 h is discussed below.

The product yields from the second set of experiments (2 through 4) are listed in Table 2. These experiments were designed to test the effect of coal rank and two selected catalytic conditions on coal conversion and product oil characteristics. Table 2 also includes the product yields from the lower rank coal (Experiment 1E) for comparison. The product yields from Experiments 1E and 2 show that the lower rank coal used in Experiment 1E was much more reactive, particularly with regard to the conversion of the asphaltenes to oil.

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The evaluation of Experiments 2 and 3 shows that the autoclave's metal surfaces have a strong catalytic effect on oil production. The results of Experiment 4 indicate that nickel very effectively catalyzes the conversion of coal to soluble products but is somewhat less effective than the autoclave surfaces in catalyzing oil production. Gas formation was remarkably low in every experiment. It appears that gas formation is proportional to oil production; the gas yield was approximately 10% of the oil yield in each experiment.

The elemental composition of the oil products is given in Table 3. The H/C atomic ratios varied from 1.13 to 1.24, and the oil from the nickel-catalyzed reaction had the highest value. The oil produced from lower rank coal (Experiment 1E) had the same H/C ratio as the oil product from the higher ranking coal (Experiment 2), even though the oil yield in Experiment 1E was 50% higher. The oil from Experiment 1E had a significantly lower oxygen content than the oil from Experiment 2. This difference may indicate that the cleavage of certain C-O bonds has an important role in oil formation.

The hydrogen-type distributions of the oil products were determined by proton NMR spectroscopy. Figure 1 shows the spectrum of the oil from Experiment 1E as an example. The integration results are presented in Table 4. In agreement with the elemental analysis data, the NMR integration values show that the oil made by nickel catalysis (Experiment 4) had significantly more saturated structures than the oil formed via catalytic effect of the autoclave surfaces (Experiment 2). These results plus the fact that the oil yield was greater in Experiment 2 than in Experiment 4 indicate that the catalytic effect of the autoclave surfaces preferentially catalyzed hydrocracking reactions leading to oil formation, while nickel catalysis resulted in more hydrogen uptake leading to the formation of saturated structures.

The oil products from Experiments 2 through 4 were further characterized by simulated distillation and by FIMS. The data indicate that there is close similarity between the structural features of the oils from Experiments 2 and 3. The presence of several homologous series (such as alkyl derivatives of phenol, diphenyl/acenaphthene, and pyrene) has been indicated in these oil products. The product oil from the nickel-catalyzed hydrogenation is quite different in that the data indicated the presence of more hydrogenated ring structures in it.

The hydrogen type distributions of an oil fraction obtained by moderate temperature hydrogenation and of distilled oil fractions of extract and process solvent samples from an integrated two-stage liquefaction pilot plant, are compared in Table 5. The oil from moderate temperature hydrogenation is much less aromatic and contains more saturated structures than the pilot plant products, which were produced at significantly higher temperatures.

SUMMARY AND CONCLUSIONS

Hydroliquefaction of two bituminous coals was explored to obtain information on the chemistry of liquefaction. Tests were conducted in the temperature range of 275 to 325°C and at 20.7 MPa hydrogen pressure. No donor solvent was added to the reactant to simplify product analysis and the evaluation of the results. The results and conclusions are summarized below:

1. Exploratory tests showed that at a liquefaction temperature of 325°C, high conversion to oil can be obtained with few side reactions resulting in gas or coke formation. Therefore, this temperature was selected to explore further the effect of coal rank and catalysis on coal conversion.

2. Of the two bituminous coals tested, the lower rank coal (C = 80%) was much more reactive and gave 50% higher oil yield than the higher rank coal (C = 82%). The oil yields were 72% and 48%, respectively.

3. It was shown in experiments made with the higher rank coal (C = 82%) that the metal components of the autoclave (liner and impeller) had a strong catalytic effect on the liquefaction reaction. When the metal parts of the autoclave were replaced with a glass-coated liner and impeller, the oil yield was reduced from 48% to 19%.

4. Catalysis by nickel, applied as nickel acetate impregnated into the coal, gave significantly different results from those obtained in the metal-lined reactor. Overall conversion to soluble products was higher using the nickel catalyst (94% versus 87%). However, nickel catalysis gave lower conversion to oil (40% versus 48%).

5. The oil produced in the nickel-catalyzed hydrogenation was significantly more aliphatic in character than the product from the metal-surface catalyzed reactions. The aliphatic to aromatic proton ratios were 83/17 and 74/26, respectively. Also, the nickel-catalyzed product had a much higher $(\beta + \gamma)/\alpha$ aliphatic proton ratio than the metal-catalyzed product (55/28 versus 43/32). These data indicate that nickel catalysis strongly promoted hydrogenation of aromatic rings while the metal components more effectively catalyzed hydrocracking reactions, which resulted in oil formation.

ACKNOWLEDGEMENTS

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TABLE 1

TEST CONDITIONS AND PRODUCT YIELDS

| Experiment | Temperature (°C) | Pressure (MPa) | Time (h) | Conversion (% daf Coal) | | Product Appearance |
				Gas	THF Soluble	
Untreated coal	-	-	-	-	5	Dry powder
1A	272	20.0	1.0	0.4	8	Dry powder
1B (D$_2$)	271	20.3	1.0	0.3	15	Dry powder
1C	310	20.7	1.0	1.0	22	Black solid
1D	325	19.3	1.0	1.7	29	Shiny black solid
1E	325	19.3	48.0	5.8	77[a]	Thick dark oil

[a]Most of this THF-soluble product was hexane-soluble oil (72% based on daf coal).

TABLE 2

PRODUCT DISTRIBUTIONS FROM MODERATE TEMPERATURE
LIQUEFACTION EXPERIMENTS[a,b]

Experiment	1E	2	3	4
Coal rank % C, daf	80	82	82	82
% 0 daf	9.6	7.1	7.1	7.1
Catalyst	Yes (Liner/ impeller)	Yes (Liner/ impeller)	No	Yes (Nickel- acetate)
Conversion	84	87	80	94
Product yields:				
Gas	6	4	3	4
Oil	72	48	19	40
Asphaltene	6	18	33	28
Preasphaltene	1	17	25	22
Residue	16	13	20	6

[a]All hydrogenation experiments made at 325°C, ~20 MPa, and using 48-h reaction time.
[b]Percent on loss-free, daf-basis.

TABLE 3

ELEMENTAL COMPOSITIONS OF PRODUCT LIQUIDS

Sample	Composition (wt. %)						
	C	H	N	O	S	Total	H/C
Experiment 1E, oil	88.2	8.4	1.1	1.8	0.6	100.1	1.14
Experiment 2, distilled liquid	86.3	8.1	1.2	3.6	0.4	99.6	1.13
Expermiment 2, oil	86.1	8.2	0.9	4.2	0.4	99.8	1.14
Experiment 3, oil	87.2	8.6	0.8	2.7	0.7	100.0	1.18
Experiment 4, oil	86.5	8.9	0.9	2.7	0.6	99.6	1.24

TABLE 4

PROTON NMR INTEGRATION VALUES

Hydrogen Type	Chemical Shift (ppm)	Experiment Number				
		Hydrogen-Type Distribution (%)				
		1E (Oil)	2 (Liquid)	2 (Oil)	3 (Oil)	4 (Oil)
Condensed aromatic, 4+ rings	7.85	4.0	2.5	3.1	1.5	1.4
Condensed aromatic, 2-3 rings	7.2-7.85	10.1	10.4	10.5	7.7	6.4
Aromatic single ring	6.8-7.2	4.7	6.7	6.6	6.8	5.4
Phenolic OH	6.3-6.8	1.4	5.2	7.2[a]	2.8	3.1
α^2-aliphatic	3.7-4.2	1.8	2.1	0.9	1.1	0.6
α-aliphatic	2.0-3.7	33.9	30.7	29.7	32.3	28.5
β-aliphatic	1.0-2.0	35.4	34.4	33.2	36.9	39.3
γ-aliphatic	0.5-1.0	8.7	8.0	8.8	10.9	15.3

[a]Includes 2.3% contribution from 4.2 to 5.2-ppm region.

TABLE 5

MODERATE TEMPERATURE VS TWO-STAGE LIQUEFACTION-COMPARISON OF HYDROGEN TYPES

Oil Product From	Yield (%)	Hydrogen Distribution (%)		Aliphatics		
		Condensed Aromatic	Single Ring Aromatic	α	β	γ
Moderate temperature liquefaction[a]	72	14	6	36	35	9
Two-stage liquefaction[b]						
Extract[c]	41	27	14	28	29	4
Process solvent[c]	48	26	10	24	35	3

[a]Pittsburgh seam coal, C = 80.1%
[b]Illinois No. 6 coal, C = 79.2% (from Ref. 4)
[c]-454°C distillate
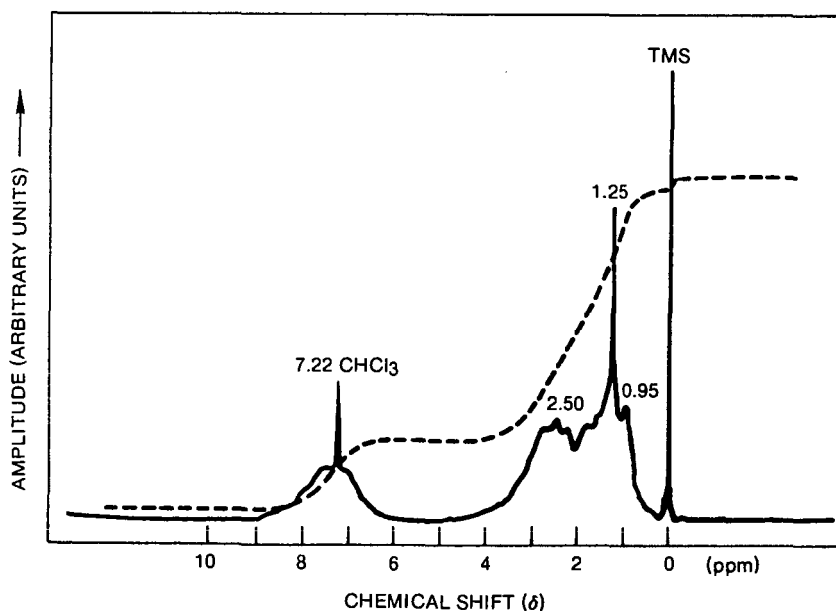
COAL PROCESSING IN NON-DISSOLVING MEDIA

Myron Kaufman, W. C. L. Jamison, S. Gandhi and Dennis Liotta

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Introduction

If coal is contacted with an organic reagent in a medium in which the reagent is marginally soluble, there may be a tendency for the reagent to transfer to the pores and surfaces of the coal, where it has maximum utility for reactions which cleave the coal macromolecular network. Thus, in such media it may be possible to employ lower concentrations of reagents than would be required in totally soluble systems. If, in addition, coal fragments are insoluble in the processing medium, the coal particles will be recovered intact after processing. The reagent can then be washed from the coal, and coal conversion assessed as solubility in a standard solvent. Since the reagent is not present when solubility is measured, conversion should be independent of the solvent properties of the reagent, and only dependent on its ability to break bonds during processing. In our work, we have focused on the reagent 1,2,3,4-tetra-hydroquinoline (THQ), which has the unusual ability to disrupt coal macromolecules under mild conditions (200-250°C). A number of previous workers have commented on the efficacy of THQ as a coal solvent and have attributed it to either the basicity or the hydrogen-donating property of this molecule (1-3). Two types of non-dissolving media, perfluorocarbon liquids and water, have been employed in our studies.

Experimental

The perfluorocarbon liquids used in our experiments are typified by FC-70 (3M Corp.), a mixture of perfluorinated tertiary aliphatic amines, with a boiling point of 215°C. FC-70 has high solubility for gases such as H_2 and CO, but very low room temperature solubility for both polar and nonpolar organic molecules. Recently, we have performed some experiments in water, which is an interesting medium, since its solubility properties can be varied by adjusting pH.

Three very different coals, with the properties given in Table 1, are used in our experiments. Typically, 0.5g of coal, 0.1g of THQ and 7 ml of FC-70 or water are heated in a stainless tubing bomb under 8 MPa of H_2. Detailed procedures for carrying out the reactions and for removal of THQ before measuring the pyridine solubility of the coal have been given (4,5). Model compound studies were carried out in FC-70 with roughly equal weights of the model compound and THQ (or other reagent). The occurrence and nature of reaction was assessed by thin layer chromatography and 90 MHz proton NMR.

Table 1. Coal Properties

PSOC Designation	1104	247	1098
Moisture (%)	1.95	30.36	4.19
Ash (% on dry basis)	3.43	11.29	15.86
Volatile Matter (% MAF)	43.83	46.22	41.78
C (% MAF)	84.47	74.44	80.20
H (% MAF)	5.66	4.93	5.73
N (% MAF)	1.46	1.49	5.73
S (% MAF)	1.86	0.53	4.73
O (by difference)	6.48	18.61	7.89

1104 - HVA bituminous coal from Elkhorn #3 Seam
247 - North Dakota lignite A from Noonan Seam
1098 - Illinois #6 coal

Results

As previously reported, the pyridine solubilities of three very different coals were increased to 33-35% by long-term (18 hour) heating at 250°C with THQ in FC-70. For each coal, the kinetics were first-order with rate constant of ca. 0.6 hr^{-1}, and not mass-transport limited, as indicated by lack of dependence on particle size. A number of other reagents were evaluated concerning their ability to increase coal conversion under the mild conditions employed in these experiments. Quinoline, diethylamine, triethylamine, ethylenediamine and tetralin all produced less than 6% increase in the pyridine solubility of a bituminous coal heated at 250°C for 4 hours, while THQ produced almost a 20% increase under these conditions.

In order to determine the nature of the bonds in coal that were being cleaved by THQ under our mild conditions, a number of model compounds were heated with THQ in FC-70 under conditions identical to our coal experiments. These model compounds consisted of phenyl groups connected by various linkages that have been discussed as being of some importance in the coal macromolecular structure. The results of these studies are given in Table 2. For the two model compounds for which reaction was noted (diphenyldisulfide and phenyl benzoate), the reactions with tetralin and diethylamine were also investigated.
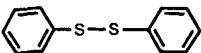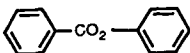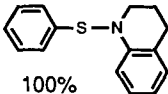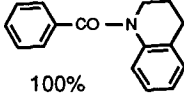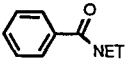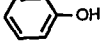
Two other media were employed to help understand the effectiveness with which small additions of THQ increase coal conversion in perfluorocarbon liquids. Dodecane has a similar boiling point to FC-70, but considerably greater solubility for THQ. It is probably only an effective extraction medium for free saturated hydrocarbons in coal. Water, on the other hand, while it has very low solubility for THQ, can dissolve strongly polar and highly acidic or basic components of coal. When bituminous coal was treated with THQ at 250°C for 4 hours in dodecane only 2% increase in coal pyridine solubility was obtained. With neutral pH water the results were very similar to what was obtained with FC-70. Very little of the coal dissolved in the water, as indicated by its light color. However, after washing out the THQ and water, the pyridine solubility of the coal was found to have increased by ca. 20%, a value very close to that achieved with THQ under similar conditions. Somewhat different results were obtained when a strongly basic (ca. 1M NaOH) solution was employed. In this case, the aqueous phase was very dark, but the remaining coal had only the pyridine solubility of unprocessed coal.

Discussion

Comparison of the results in FC-70, water and dodecane indicate that it is the marginal solubility of THQ in the first two of these media that permits low concentrations of this reagent to produce substantial increases in coal solubility. We envision that in FC-70 and water, THQ selectively transfers into the pores and onto the surfaces of the coal, while in dodecane it maintains a more uniform and low concentration throughout the system.

Although the model compound studies have not probed all possible bonds in coal macromolecules, our results suggest that only ester and disulfide bonds are susceptible to attack by THQ under the mild conditions of our experiments. In both cases the initial mode of reaction appears to be nucleophilic attack by the nitrogen lone pair, followed by bond scission and hydrogen donation in either a concerted or successive manner. Since tetralin is not a nucleophile, it cannot initiate similar reactions. The thiol produced with tetralin and diphenyldisulfide probably results from thermal scission of the disulfide, followed by hydrogen abstraction by the thio radical. Small amounts of thiol are formed when the tetralin is omitted in this experiment. In this case, with only H$_2$ available as a hydrogen donator, many of the thio radicals probably recombine. Since ester bonds are considerably stronger than disulfide bonds, it is not surprising that there is little reaction between tetralin and phenyl benzoate at 250°C. Diethylamine should be a more potent nucleophile than

TABLE 2 MODEL COMPOUND STUDIES

Substrates

Reactants	⟨◯⟩–S–S–⟨◯⟩	⟨◯⟩–CO₂–⟨◯⟩
THQ	⟨◯⟩–S–N(tetrahydroquinoline) 100%	⟨◯⟩–CO–N(tetrahydroquinoline) 100%
Tetralin	⟨◯⟩–SH 100%	No Reaction
Diethylamine	50 % substrate recovered *	⟨◯⟩–C(=O)–NET₂ + ⟨◯⟩–OH 100%

Conditions: 4 hrs at 250 C in FC-70 with 7 MPa H₂.

* Black, insoluble material was formed

The following substrates did not react with THQ under these conditions:

⟨◯⟩–CH₂CH₂–⟨◯⟩   ⟨◯⟩–S–⟨◯⟩   ⟨◯⟩–CH₂SCH₂–⟨◯⟩

⟨◯⟩–CH₂OCH₂–⟨◯⟩   ⟨◯⟩–CO–⟨◯⟩   ⟨◯⟩–CH₂COCH₂–⟨◯⟩
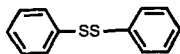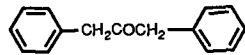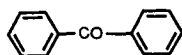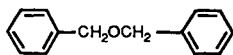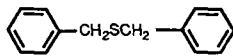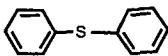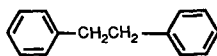
⟨◯⟩–SS–⟨◯⟩   produced 15 % thiophenol when all reactants were omitted

THQ, and indeed it does react with both diphenyldisulfide and phenyl benzoate at rates comparable to THQ. (The product of the disulfide reaction is a black, insoluble material that we have not yet been able to identify.)

In attempting to chose between esters and disulfides as the predominant bonds broken by THQ in our experiments, we must rationalize the observed attack of diphenyldisulfide by tetralin and both diphenyldisulfide and phenyl benzoate by diethylamine, while neither of these reagents are substantially effective in increasing coal solubility. Since tetralin has a similar boiling point and aromaticity to THQ, it is very difficult to explain the tetralin results if disulfide bonds are predominant. Diethylamine, however, with its lack of aromatic character, might find the coal environment much less favorable for selective partitioning. In addition, the high volatility of diethylamine would result in a substantial partitioning into the gas phase. Thus, the ineffectiveness of diethylamine with coal can be rationalized, and we prefer ester bonds as the primary linkages being attacked in our coal experiments. The surprising result that three very different coals all achieved very similar ultimate solubility upon long-term reaction with THQ in FC-70 at 250°C could most easily be explained by the postulate that these coals in their early stages of development all had similar concentrations of ester bonds in their macromolecular networks. At the so-called first coalification step, which occurs at ca. 78% carbon, coals lose CO_2, much of which comes from ester bonds, and the destruction of these bonds could account for the higher initial solubilities of PSOC 1098 and 1104. Van Bodegam et al. have reported that while low-rank coals contained ester bonds that could be broken in reactions with primary amines at temperatures of 120–180°C, no such bonds were found in medium and high-rank coals (6). Our work suggests that there are additional ester bonds in medium-rank coals that can be attacked by THQ at 250°C.

In both FC-70 and water, the amides generated by reaction of THQ with ester bonds in coal would show very little solubility, and thus it is not surprising that the coal does not dissolve in these media. With strongly basic water, however, further saponification of the amide occurs, with ionization of the resulting acids. The aqueous phase in this experiment therefore dissolves large concentrations of the coal fragments.

Acknowledgment

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EXTRACTION OF LOW-RANK COALS WITH SUPERCRITICAL WATER

M.L. Swanson, E.S. Olson, J.W. Diehl, and S.A. Farnum

University of North Dakota Energy Research Center
Box 8213, University Station
Grand Forks, ND 58202

Abstract

Supercritical water extractions were performed on low-rank coals utilizing a semicontinuous supercritical solvent extraction system. Percent conversions ranged from 40% to 50% while extract yields ranged from 10% to 30% at 380°C. The conversions and extract yields increased with increasing operating temperature and pressure. The conversions also decreased with increasing coal rank and correlated well with the percent volatile matter in the coals.

Organic analyses of the resulting extracts have included separations into pentane, methylene chloride and methanol soluble fractions by short column chromatography, 200 MHz proton NMR, IR spectroscopy and capillary gas chromatography. Proximate and ultimate analyses indicated that supercritical water extracts the volatile, hydrogen-rich fraction of the coal. Organic analyses show that the extract is highly polar in nature with significant quantities of phenols and long-chain aliphatic fatty acids.

Introduction

Interest in the extraction of solutes with supercritical solvents has been increasing rapidly over the past fifteen years. This interest is primarily due to the enhanced solubility of substrates in the fluid phase that occurs at or above the critical point. It has only been in the last few years that considerable research has addressed the use of supercritical water as a solvent suitable for obtaining high yields of environmentally acceptable fuels and chemical feedstocks from coal (1, 2, 3). Under ambient conditions, organics and water are generally immiscible. However, as water approaches its critical point, the solubility of organics in water increases drastically (4, 5) while the solubility of inorganics in water substantially decreases (6). These solubility changes contribute to the potential of supercritical water to obtain high yields of relatively ash-free hydrocarbons from coal. In addition, other investigations have shown the potential for increasing supercritical water yields even further through the addition of a reducing agent such as CO or H_2S to the supercritical water system (7, 8, 9).

The objective of this research was to investigate the use of water as a cheap supercritical extraction solvent for obtaining environmentally acceptable liquid fuels and chemical feedstocks from coal and attempt to use supercritical solvent extraction as a means for determining the composition of various molecular fractions present in low-rank coals.

Experimental Procedure

Supercritical water extractions were performed using a semicontinuous extraction system in which deionized water under supercritical conditions was passed through a fixed bed of coal. The coals used in this experiments included the Indian Head, Center, and Martin Lake lignites along with Sarpy Creek and Wyodak subbituminous coals. Proximate and ultimate analyses for these coals are shown in Table I. As shown in Table I, there was a difference between the beginning and ending samples of the Indian Head lignite used in these experiments. Figure 1 is a flowsheet of the supercritical solvent extraction system as it was used for most of the supercritical water experiments. In this system, a fixed bed of coal was detained by sintered metal frits in a horizontal section of high pressure tubing. A rehabilitated GC

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TABLE I. Proximate and Ultimate Analyses of Coals Used in Supercritical Water Experiments

	Indian Head 1 Mercer Co., ND	Indian Head 2 Mercer Co., ND	Center Oliver Co., ND	Martin Lake Panola Co., TX	Wyodak Campbell Co., WY	Sarpy Creek Big Horn Co., MT
				Sample Name and Location		
Proximate Analysis (wt%)						
Volatile Matter	43.8	49.8	43.0	42.2	43.5	34.8
Fixed Carbon	48.0	41.9	48.6	42.8	50.0	45.4
Ash	8.2	8.3	8.4	15.0	6.5	19.8
Ultimate Analysis (wt%)						
Hydrogen	4.74	4.45	4.13	0.32	4.26	3.64
Carbon	66.20	64.96	64.07	61.88	64.62	59.43
Nitrogen	0.96	1.00	1.13	1.23	1.01	0.83
Sulfur	0.72	0.33	1.16	1.17	0.58	4.22
Oxygen (Ind)	19.19	20.96	21.08	20.40	23.04	12.11
Ash	8.2	8.3	8.42	15.0	6.5	19.8

oven was used to heat the solvent and extraction vessel to temperature at 20°C/min., after which a pulseless flow of solvent was started through the system. The extracted organics and solvent then passed through a back pressure regulator where the precipitated extract was collected in a heated sample cylinder while the vaporous solvent and light gases were collected in chilled sample vessels. The volume of noncondensable product gas was measured and collected for analysis.

Analytical Procedure

After each experiment, any water remaining in the extract sample cylinder was filtered from the solid extract and selected samples of the recovered water solvent were analyzed by gas chromatography for their concentrations of water soluble organics. The solid extract was washed from the sample cylinder with acetone and the extracted coal residue and solvent-extract mixture were then rotary vacuum distilled to remove the solvent. This procedure allowed a relatively moisture-free product to be obtained for material balance purposes. Residues were analyzed by thermogravimetric analysis (TGA) and proximate and ultimate analyses were performed on selected samples.

Discussion and Results

The operating conditions and the corresponding results of these supercritical water extractions are shown in Tables II and III. The effect of extraction time on percent conversions is shown in Figure 2. This figure indicates that the percent conversions increase linearly with an increase in coal residence time up to approximately 45 minutes after which the conversions leveled off at ~42% to 43%. A vacuum dried sample (0.65 wt% moisture) was also extracted for 60 minutes with supercritical water at similar operating conditions and resulted in a 33.5% conversion. This lower conversion was due to a sample size effect since drying the coal resulted in a 60% larger sample of maf coal being extracted. A conversion of 44.2% was obtained for a separate run using a vacuum dried coal at longer residence times which indicated that no advantage resulted in extracting "as received" coals with their inherent moisture already present in the sample's porous structure. Also, considering that a 33% larger sample of maf coal was being extracted, the slightly higher conversions obtained for the supercritical water experiment performed at a flow rate of 240 cc/hr suggests that an increase in the solvent flow rate increased the rate of extraction.

The effects of operating temperature and pressure on the resulting conversions was investigated using operating temperatures of 380°C or 440°C (Tr = 1.01 or 1.10) while the operating pressures used were 3265, 4013, or 4815 psia (Pr = 1.02, 1.25, 1.50). Results of these experiments are summarized in Table II. Figure 3 is a plot of the reduced pressure versus the percent conversion at both operating temperatures. This figure indicates that a small increase in the conversions was obtained with an increase in the operating temperature. The conversion also displayed a larger increase with increasing pressure up to 4000 psia. Above 4000 psia, there appeared to be no effect on the resulting conversions. This increase in conversions is the result of a large increase in solvent density caused by the increased pressure. The increase in conversion with higher temperature was the result increasing thermal decomposition or reactions of the lignite in this temperature region. The product gas compositions and yields appeared to be only temperature and coal dependent and were not affected to any large degree by operating pressure or solvent flow rate.

Table III shows the effect coal rank had on the percent conversion obtained using supercritical water at 380°C and pressures of either 3265 or 4013 psia. For comparison purposes, supercritical water experiments were also performed on a Red Lake Peat and a biomass sample and the results are also displayed in Table III. These results suggest that there is a high degree of correlation between the percent conversions obtained using supercritical water and the amount of volatile matter present in the starting coal. This finding is consistent with results reported by Great Britain's National Coal Board in which percent conversions using supercritical

TABLE II. Operating Conditions and Results from Supercritical Water Extractions of Indian Head Lignite

Coal	Temp (°C)	Tr**	Pressure (psia)	Pr**	Solvent Density (g/cc)	Solvent Flowrate (g/cc)	Residence Time (min)	Percent Conversion (MAF)+	Extract Yield (MAF)*	Volatile Yield (MAF)*	Product Gas Yield*
Indian Head (as received)	380	1.009	3265	1.017	.193	120	15	25.2	8.0	0.2	5.5
Indian Head (as received)	380	1.009	3265	1.017	.193	120	30	34.3	10.4	1.4	10.4
Indian Head (as received)	380	1.009	3265	1.017	.193	120	45	43.1	10.1	2.2	9.6
Indian Head (as received)	380	1.009	3265	1.017	.193	120	60	42.7	22.6	ND	12.5
Indian Head (vacuum dried)	380	1.009	3265	1.017	.193	120	60	33.5	8.5	1.8	11.4
Indian Head (as received)	380	1.009	3265	1.017	.193	120	80	42.6	12.0	2.9	11.6
+Indian Head (as received)	380	1.009	3265	1.017	.193	240	30	36.0	9.9	2.1	8.0
+Indian Head (as received)	380	1.009	3265	1.017	.193	120	240	43.3	18.8	2.5	10.8
+Indian Head (as received)	380	1.009	4013	1.250	.504	120	240	50.6	22.4	2.3	12.6
Indian Head (as received)	380	1.009	4815	1.500	.558	120	240	50.3	23.8	2.9	12.1
+Indian Head (as received)	440	1.102	3265	1.017	.097	120	240	43.3	13.3	ND	19.3
+Indian Head (as received)	440	1.102	4013	1.250	.137	120	240	53.2	21.1	ND	17.0
Indian Head (as received)	440	1.102	4815	1.500	.199	120	240	54.4	21.8	ND	16.3
Indian Head (vacuum dried)	380	1.009	3265	1.017	.193	120	150	44.2	12.2	2.3	16.7

* % conversion = $\dfrac{\text{wt maf coal} - \text{wt maf residue}}{\text{wt maf coal}}$; % yield = $\dfrac{\text{wt maf product}}{\text{wt maf coal}}$

+ - average value
ND - not determined

** Tr = $\dfrac{\text{operating temperature of solvent (°K)}}{\text{critical temperature of solvent (°K)}}$; Pr = $\dfrac{\text{operating pressure of solvent (psia)}}{\text{critical pressure of solvent (psia)}}$

TABLE III. Operating Conditions and Results from Supercritical Water Extractions of Low-Rank Coals

Coal	Temp (°C)	Tr**	Pressure (psia)	Pr**	Solvent Density (g/cc)	Solvent Flowrate (g/cc)	Residence Time (min)	Percent Conversion (MAF)	Extract Yield (MAF)*	Volatile Yield (MAF)*	Product Gas Yield*
Coal Type Experiments											
Center	380	1.009	3265	1.017	.193	120	60	43.4	24.6	ND	ND
Martin Lake	380	1.009	4013	1.250	.504	120	150	45.2	20.2	1.7	12.1
Wyodak	380	1.009	3265	1.017	.193	120	150	33.7	14.0	ND	14.5
Wyodak	380	1.009	4013	1.250	.504	120	150	39.5	15.0	1.6	22.4
Sarpy Creek	380	1.009	4013	1.250	.504	120	150	33.5	21.2	1.3	3.6
Red Lake Peat	380	1.009	3265	1.017	.193	120	60	75.8	25.6	3.6	20.5
Biomass (Douglas Fir Sawdust)	380	1.009	3265	1.017	.193	120	60	83.8	33.7	3.6	33.6
Lithotype Experiments											
Indian Head Vitrain (50% of original)	380	1.009	3265	1.017	.193	120	60	42.3	22.2	6.9	6.7
Indian Head Durain (45% of original)	380	1.009	3265	1.017	.193	120	60	39.8	18.0	1.8	7.6
Indian Head Fusain (5% of original)	380	1.009	3265	1.017	.193	120	60	32.3	28.1	0.4	4.7
Special Run											
Indian Head (w 90% H_2O-10% CO)	383	1.003	3300	ND	ND	120+CO	60	41.2	12.3	2.1	NA

* % conversion = $\dfrac{\text{wt maf coal} - \text{wt maf residue}}{\text{wt maf coal}}$; % yield = $\dfrac{\text{wt maf product}}{\text{wt maf coal}}$

+ - average value
ND - not determined

** Tr = $\dfrac{\text{operating temperature of solvent (°C)}}{\text{critical temperature of solvent (°K)}}$; Pr = $\dfrac{\text{operating pressure of solvent (psia)}}{\text{critical pressure of solvent (psia)}}$

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toluene also correlated well with volatile matter of the original coal (10). As a result, the conversions decreased with an increase in coal rank. This increase in conversions which occurred is the result of the increased concentration of thermally laible carbohydrate, lignin or lignin-derived components which exist in the lignite, peat, and biomass.

Supercritical water extractions of the Indian Head lithotypes; vitrain, durain, and fusain were performed. Approximately 12 to 15 grams of each lithotype were microscopically separated. The conversions obtained for the vitrain and durain fractions (which make up approximately 50 and 45 wt% of the original Indian Head) were found to be similar to those obtained using the original Indian Head lignite as shown in Table III. Table III also shows that the conversion of the fusain portion (∿5% of the original Indian Head) was significantly less than that for the original lignite. These results agree with other reported results in which vitrains and durains have been found to be highly susceptible to liquefaction, (i.e., susceptible to thermal cleavage and reaction with hydrogen) while fusain has been found to behave as more of an inert material (11). The yields of water-soluble organics from these lithotypes and the original lignite are shown in Table IV. As shown, the vitrain fraction contains considerably more of the oxygenated water-soluble volatile compounds (i.e., acetone, methanol, and phenol) than the original Indian Head, while the durain fraction contains slightly less of these compounds than the original lignite. The concentrations of these compounds in the fusain fraction were very small compared to that of the original lignite.

TABLE IV. Percent Yields of Volatile Components Found in Recovered Supercritical Water Solvent

| | Supercritical Water Extraction | | | | |
Component	Indian Head 2	Sarpy Creek	Indian Head Vitrain	Indian Head Durain	Indian Head Fusain
Phenol	0.63	0.21	1.14	0.48	0.14
o-Cresol	0.17	0.06	0.20	0.10	0.05
m,p-Cresol	0.17	0.13	0.22	0.18	0.05
Total Phenolics	0.97	0.40	1.56	0.76	0.24
Methanol	0.80	0.04	1.32	0.22	--
Acetone	0.91	0.42	3.93	0.70	0.15
MEK	0.25	0.10	0.12	0.14	0.05
Total	2.93	0.96	6.93	1.82	0.44

As shown in Table III, a special experiment was performed using a 90-10 mole% mixture of water-carbon monoxide to extract Indian Head lignite at 383°C and 3300 psia. The purpose of this experiment was to determine what effects the addition of a reducing gas such as CO has on the molecular composition of the extract. The conversion and yields obtained were similiar to those obtained for an experiment using pure water under similar conditions.

Results From Analysis of Supercritical Water Residues and Extracts

Proximate and ultimate analyses of selected residues and extracts from supercritical water and the original Indian Head are shown in Table V. The proximate analysis indicates that the supercritical water extract contains a significantly higher fraction of volatile matter while the residue contains a significantly lower fraction of volatile matter than the original Indian Head. The

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TABLE V. Comparison of Proximate and Ultimate Analyses of Supercritical Water Residues and Extracts to the Original Sample

Sample Description - All Samples run at 380°C, 3265 psia, 120 cc/hr

	Indian Head Water - 30 min		Indian Head Water - 60 min		Indian Head Water - 60 min		Original Red Lake Peat Sample	Red Lake Peat Water - 60 min		Original Biomass Sample	Biomass Water - 60 min	
	Residue	Extract	Residue	Extract	Residue	Extract		Residue	Extract		Residue	Extract
Percent Conversion (MAF)	34.3		42.7		41.2		NA	74.7		NA	83.8	
Percent Extract Yield (MAF)	10.4		22.6		12.3		NA	26.1		NA	33.7	
Proximate Analysis (MF)												
Volatile Matter	27.8	71.3	30.4	79.8	27.6	99.6	67.4	23.6	97.9	85.4	35.2	97.5
Fixed Carbon	63.8	26.7	61.0	19.8	60.7	0.4	12.9	32.8	1.9	13.2	62.0	2.5
Ash	8.4	2.0	8.6	0.4	11.7	0.0	19.7	43.6	0.2	1.4	2.8	0.0
Ultimate Analysis (MF)												
Hydrogen	3.67	7.67	3.53	7.63	3.41	9.01	2.62	2.52	8.51	6.55	3.62	6.28
Carbon	73.81	78.10	75.10	78.73	72.55	66.44	54.99	44.98	74.66	52.48	77.92	72.09
Nitrogen	1.34	0.69	1.38	0.84	1.40	0.72	2.89	2.22	2.80	0.40	0.75	0.71
Sulfur	0.42	1.42	0.38	0.42	0.39	0.30	0.31	0.25	0.15	0.09	0.13	0.08
Oxygen (Ind.)	12.36	10.11	11.01	11.97	10.54	23.53	19.49	6.43	13.67	39.09	14.78	20.84
Ash	8.4	2.0	8.6	0.4	11.7	0.0	19.7	43.6	0.2	1.4	2.8	0.0

ultimate analysis shows that the extract had a lower C/H ratio than the original Indian Head whereas the residue had a higher C/H ratio than the original Indian Head. These analyses indicate that the hydrogen-rich, lower molecular weight portion of the lignite is being extracted while leaving a highly carbonaceous residue.

The analyses also indicate that the mineral matter is concentrated in the residue while a relatively ash-free extract is obtained. Table V compares the proximate and ultimate analyses of the residues and extracts for runs using supercritical water and the supercritical water-CO mixture. The C/H ratio is substantially lower for the run using the H_2O-CO mixture which suggests the possible addition of H_2, which was generated by the water-gas shift reaction, to the extract.

Thermogravimetric analyses were performed in argon on samples of the original coal and supercritical water residues using a heating rate of 20°C/min. and a final temperature of 900°C. The weight-temperature profiles indicated that ~20 wt% of the supercritical residues were volatilized while approximately 41% of the original coal would volatilize under the same conditions. The differential weight loss curves for two supercritical water residues and the original Indian Head lignite are shown in Figure 4. This figure indicates that supercritical water has extracted most of the compounds which would devolatilize below ~550°C, thus, concentrating the higher molecular weight material in the residue which results in the higher differential weight loss curve at temperatures above 550°C.

Analysis of a supercritical water extract was carried out using chromatographic separations, infrared (IR), and nuclear magnetic resonance (NMR) spectroscopy. The extract was separated into three fractions by short column chromatography on silica gel. The first fraction was separated by successive elution with pentane and then isooctane. This fraction was found to make up approximately 5% of the extract and the NMR spectra showed that this fraction consisted only of aliphatic materials. This fraction was analyzed by capillary column gas chromatography and was found to contain a series of alkanes and alkenes in the range of C-18 to C-34. The presence of the alkenes indicates that thermal cracking is occurring but the relative amounts of the alkanes alternate as the carbon chain increases in the series, which suggest that the cracking was minimal, perhaps confined to reactions near the acid or ester function. Also, the predominance of the odd-number chains and the high concentration of CO_2 in the product gas indicate that a significant amount of decarboxylation was occurring.

The second fraction was separated by elution with methylene chloride and was found to make approximately 26% of the extract. Some identified individual hydrocarbons include phenanthrene, fluorene, anthracene, pyrene, benzofluorenes, and fluoranthene. The NMR spectrum shown in Figure 5 also suggests the possible presence of ester groups between 3.8 and 4.0 ppm. The last fraction was obtained by elution with methanol and was found to make up the majority (~69-70%) of the extract. The NMR and IR spectra on this fraction indicate the presence of phenolics and long chain aliphatic acids.

Table VI shows some of the individual coal-derived compounds which have been identified and their approximate yields. These yields indicates that the identified phenolics constituted a small fraction (from ~2.9% to 0.8%) of the supercritical water extracts. The dependence of phenol yields in the extract on coal type is noticeable with the Wyodak subbituminous coal generally yielding higher concentrations of phenols in the extract. The distribution of the individual phenols is essentially identical for the three coals, indicating that they originate from the same type of substructure in the coal and that the reactions which release them during supercritical water extraction must be identical. Thus, the ratio of the phenol yields in the three coals must result from different amounts of the substructure in the coals (probably in the same ratio).

TABLE VI. Identification and Determination of Yields for Individual Compounds in Supercritical Water Extracts Obtained at 380°C and 4013 psia

Compound	Indian Head % Yields (mcf) In Extract	In Water	Wyodak % Yields (mcf) In Extract	In Water	Martin Lake % Yield (mcf) In Extract	In Water
Methanol	ND	0.649	ND	0.113	ND	0.421
Acetone	ND	0.607	ND	0.538	ND	0.568
Acetonitrile	ND	0.001	ND	0.001	ND	0.005
Methyl Ethyl Ketone	ND	0.160	ND	0.170	ND	0.176
Propionitrile	ND	0.034	ND	0.005	ND	0.020
Catechol	ND	0.202	ND	0.151	ND	0.157
Phenol	0.028	0.362	0.075	0.340	0.026	0.167
o-cresol	0.022	0.101	0.062	0.104	0.020	0.049
m-cresol	0.030	0.110	0.067	0.094	0.024	0.049
p-cresol	0.030	0.118	0.007	0.122	0.022	0.059
2,6-diMePhe	0.002	ND	0.034	ND	+	ND
2-EtPhe	0.002	ND	0.045	ND	0.010	ND
2,4-diMePhe	0.013	ND	0.045	ND	0.017	ND
2,5-diMePhe	0.019	ND	0.018	ND	0.006	ND
2,3-diMePhe	0.009	ND	0.018	ND	0.006	ND
4-McGuaigcol	0.010	ND	0.003	ND	0	ND
2,4,6-triMePhe	0.007	ND	0 +	ND	+	ND
2,3,6-triMePhe	0.001	ND	0.003	ND	0	ND
2,4,5-triMePhe	0.004	ND	0.006	ND	0.020	ND
4-Indanol	+	ND	0.007	ND	0	ND
5-Indanol	0.009	ND	0.012	ND	0.012	ND
2,3,5,6-tetraMePhe	0.001	ND	0.003	ND	+	ND
1-Napthol	0.002	ND	0.006	ND	+	ND
2-Napthol	0.009	ND	0.018	ND	0.012	ND
Total	0.198	2.343	0.426	1.638	0.155	1.670

+ - trace
ND - not detected

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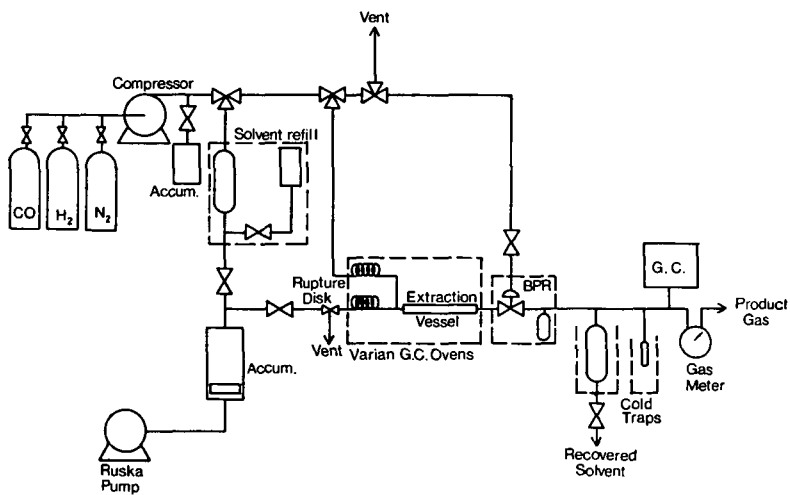
Figure 1. Flowsheet for the semicontinuous supercritical solvent extraction.
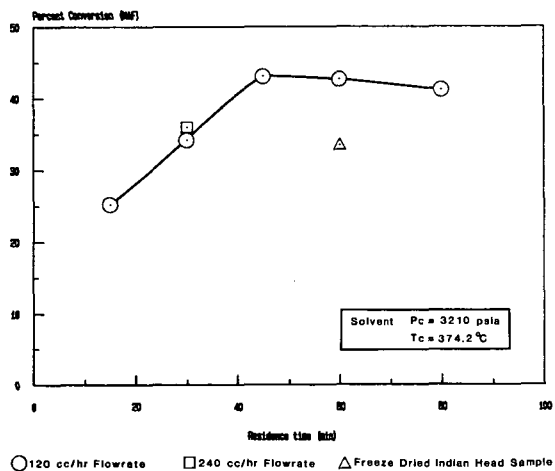
Figure 2. Extraction time and flow rate effects on supercritical water extraction.
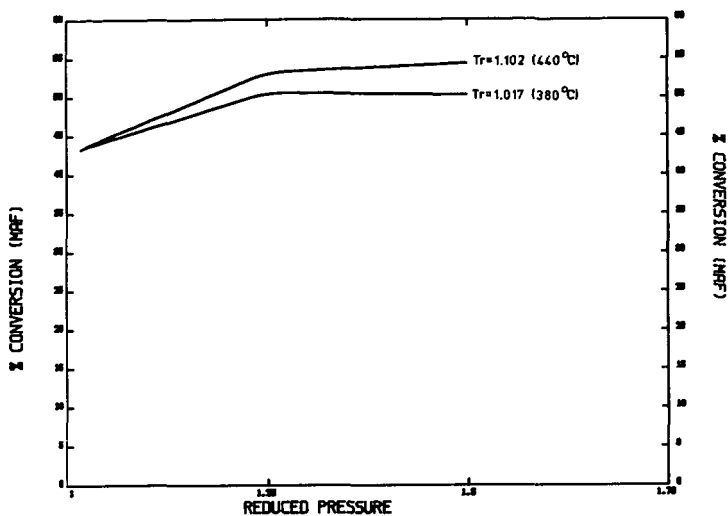
Figure 3. Effect of operating pressure and temperature on conversion of Indian Head lignite with supercritical water.
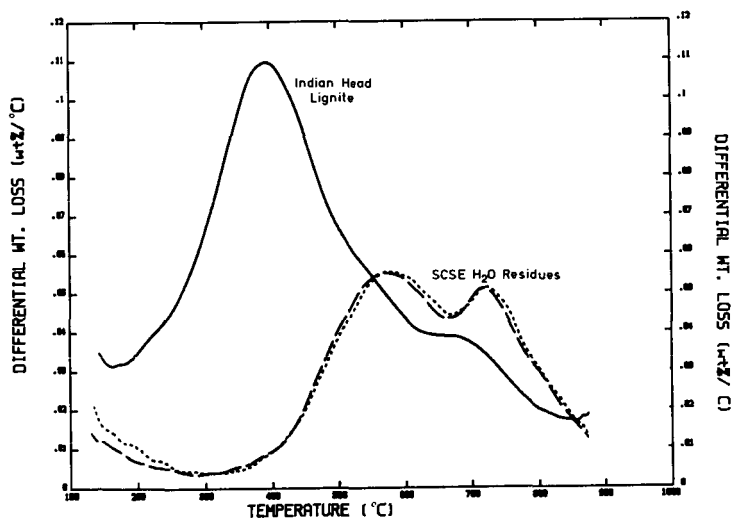
Figure 4. Differential weight loss curves for two supercritical water residues and the original coal.

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200 MHz ^{1}H NMR

Column Fractions

Pentane Eluted Fraction

Solvent

Alkanes

H$_2$O

Methylene Chloride Eluted Fraction

CH$_3$

CH$_2$

Aromatics

methyl

Methanol Eluted Fraction

Solvent

α methyl Phenols

CH$_2$

CH$_3$

Phenolic

-O-CH$_2$

δ, ppm

Figure 5. 200 MHz proton NMR of three fractions of a supercritical water extract obtained at 380°C and 3265 psia.

REACTIONS OF COAL AND COAL MODEL COMPOUNDS WITH SUPERCRITICAL WATER

MICHAEL A. MIKITA AND HOWARD T. FISH
UNIVERSITY OF COLORADO AT DENVER
DEPARTMENT OF CHEMISTRY
DENVER, COLORADO 80202

INTRODUCTION

We recently reported on the successful replacement of recycle solvent by water in conventional coal liquefaction, with and without added hydrogenation catalyst precursors (1). High coal conversions (as measured by THF solubilities) were obtained at modest temperatures (370°-385°) with the use of little or no organic recycle solvent and short reaction times (5-30 minutes).

Water has been used in the past in the liquefaction or the extraction of coal for a variety of reasons. When used in combination with carbon monoxide and a suitable catalyst, water was a source of hydrogen for the reduction of coal (2,3). Appell and co-workers frequently used an organic solvent in combination with water in these studies.

Liquefaction under carbon monoxide has also been carried out by Ross and colleagues (4,5) with slurries composed of coal and either water or aqueous base without an organic solvent. In some cases, Ross has used water to carry dissolved metal salts as homogeneous catalysts as well as a liquefaction medium (6), but still in the presence of carbon monoxide as the reducing gas.
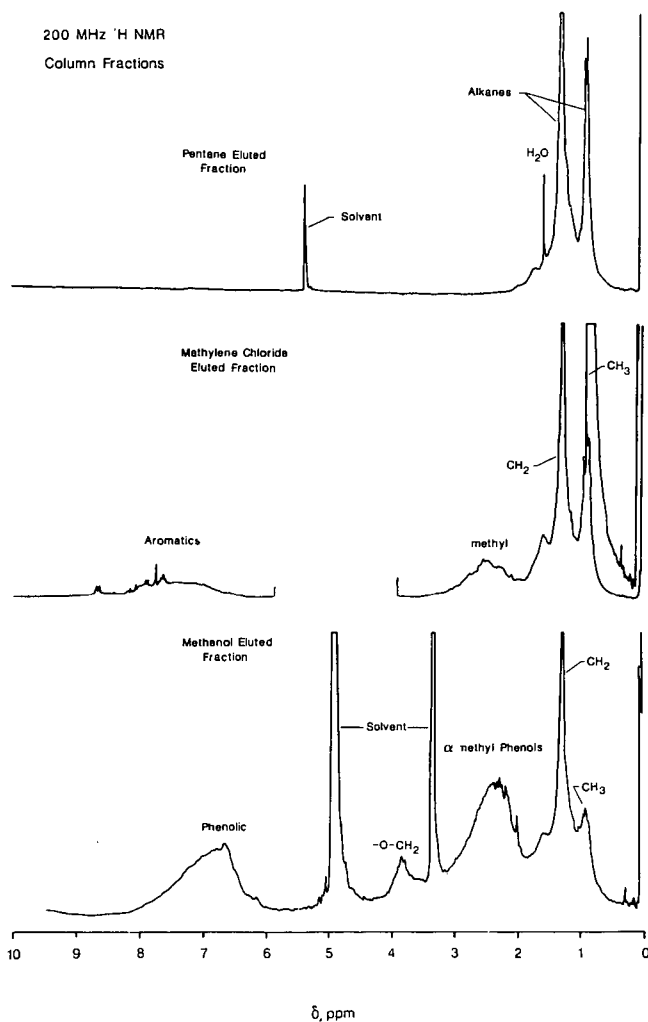
In comparison with conventional organic liquefaction solvents, Stenberg et al. have shown water to be quite effective when used in combination with H_2S, in particular under synthesis gas rather than hydrogen (7).

Aqueous liquefaction using impregnated catalysts has also been combined in a single operation with supercritical water distillation to separate the oil and asphaltene from the coal char residue (8). Barton's results clearly show that the liquids produced by hydrogenation can be extracted by supercritical water and transported away from insoluble coal residues.

Wender and co-workers have also shown that the simple treatment of coal with supercritical water in the absence of hydrogen or catalyst renders a substantial portion of the treated coal extractable by THF after the product was cooled and recovered from the autoclave (9). The amount of extract obtained depended on the density of the supercritical water. Higher yields were obtained when coal was injected into supercritical water, thus providing a rapid heat-up of the coal, than when a coal-water slurry was heated to operating temperature.

In addition to the physical role of water reported by Wender, it has also been reported that water may directly participate as a reactant in the thermolytic chemistry of certain model compounds. In the presence of water, dibenzyl ether decomposed at 400° C by both pyrolytic and hydrolytic pathways, the latter leading to the formation of benzyl alcohol (10).

The removal of nitrogen from heterocyclic compounds, such as isoquinoline, was also reported to be accelerated in the presence of supercritical water (11).

Taken together, these previous studies by other researchers indicate that under various conditions, supercritical water may act as a good liquefaction medium, dissolve or extract coal-derived liquid products, promote the cleavage of certain bonds likely to be found in coal, provide hydrogen through the water-gas shift reaction, and possibly assist the contracting of coal with catalysts or hydrogen.

Though these reports suggest a rich and varied chemistry in liquefaction with water, fundamental studies with models has received inadequate attention. The objective of this study was to initiate an investigation into the organic reaction mechanisms of coal and coal model compounds with supercritical water.

EXPERIMENTAL

A multireactor consisting of five individual microautoclaves, each of approximately 45-mL capacity and attached to a single yoke, was used to study these reactions (12). The entire assembly was immersed rapidly into a preheated, fluidized sand bath, allowing heat-up to reaction temperature in 4–6 minutes. Immersion in a second fluidized sand bath held at room temperature provided rapid quenching. The autoclaves were agitated by a rapid horizontal-shaking motion, assuring good mixing of heterogeneous, multiphase mixtures. ·Individual thermocouples allowed continuous temperature monitoring of each microautoclave. For all experiments reported here, the reactors, once pressurized, were isolated from the gas-handling manifold by a valve and a short length of tubing of negligible volume. This prevented loss of water from the reaction zone due to condensation in the unheated portion of the system. Separate experiments using different reactors, in which it was possible for water to migrate to unheated regions of the system, indicated that such water loss had a profound but erratic effect on measured values for pressure and coal conversion, and generally led to misleading data.

The pressure at reaction temperature was not measured directly in these experiments. The partial pressure of water was estimated using van der Waal's equation.

Table 1 gives the analyses of the Illinois No. 6 (River King Mine) bituminous coal and process derived solvent (SRC II). The conversion values were obtained by the centrifugation method described earlier (1).

Model compound experiments were performed in the identical reaction appartus. Any product gases were uncollected. The reactors were washed out with dichloromethane (Fisher; ACS certified) and the aqueous layer removed. The organic layer was filtered through a sintered glass funnel, with subsequent analysis by capillary gc/ms (Hewlett Packard model 5790A gas chromatograph equipped with a Hewlett Packard model 5970A mass selective detector). Mass spectral ionization currents and gc parameters were identical in the analysis of standards and reaction products.

All model compound experiments were reacted at 385° C for 30 minutes. A 1200 psig cold charge of H_2 was employed in each experiment utilizing molecular hydrogen. The bibenzyl reactions used 2.5g (0.014mol) bibenzyl (Aldrich) and 1.8g (0.09 mol) deuterium oxide (Aldrich, gold label). The biphenyl experiments also employed 2.5g (0.016 mol) biphenyl (Aldrich) and 1.8g D_2O. The reactions with 4-benzylphenol (Chemical Sales Co.), dibenzyl ether (Aldrich) and benzyl ethyl ether (Pfaltz & Bauer), used 0.92 (0.005 mol), 0.99g (0.005 mol), and 0.68g (0.005 mol) respectively, and 4.0g D_2O in each reactor.

RESULTS AND DISCUSSION

I. Bituminous Coal Studies

Inverse isotope effects has been observed by Appell (13) and Ross (14) when water was replaced with D_2O in coal liquefaction. Appell observed an enhanced conversion of nearly 6% when D_2O was utilized in place of water with hexahydropyrene (HHP) as a solvent. A significant enhancement was similarly observed by Ross through substitution of water by D_2O in his use of CO/water systems without a solvent. Ross has attributed this phenomenon to a phenol-keto equilibrium followed by hydride transfer from formate to coal moieties in a Michael sense. The inverse isotope effect, in Ross' argument, results from the fact that the formate reaction with water experiences a normal isotope effect and is therefore slowed in D_2O, consequently enhancing the stability of active formate by precluding the termination reaction to CO_2 and H_2, which he suggests rapidly prevails under these conditions.

Ross further contends that all coal liquefaction reactions can be viewed along similar lines. Donor solvent liquefaction, in his concept, results via hydride transfer from hydroaromatic compounds to effect reductions of quinones and/or semiquinones with subsequent elimination of substitutent groups.

If the mechanism of liquefaction is indeed ionic, water may be envisioned as a polar solvent, resulting in a lowering of the transition state energy via solvation and correspondingly increased conversions. With this discussion in mind, we undertook two sets of experiments, each comparing H_2O with D_2O. The first was essentially a repeat of Appell's experiment with minor variations. Tetralin was employed as the solvent and a higher hydrogen charge was utilized. In an attempt to enhance the ionic character of these reactions, 2mmol of Cs_2CO_3 was added to the water. Ross had utilized the observed catalytic effect of bases in his reactions as a major argument for his proposal of an ionic mechanism. Cs_2CO_3 was chosen since Cs has been reported as the most mobile of the Group IA metals in the gasification of coals (15) and we wished to circumvent, as far as possible, any anomalies from selected ion exchange.

The conversions obtained were identical, within experimental error, as illustrated in Table 2 (68-70 wt. %). Clearly, under these conditions, no isotope effect is evident. It is significant that Appell's work, at much lower hydrogen pressure and 5 fewer minutes residence time, resulted in dramatically higher conversions (84-90 wt. %). The greater ease of hydrogen abstraction from HHP than tetralin is dramatically evidenced by these results. These results do little, however, to support the role of water as reactant in our systems, or an ionic mechanism for liquefaction in general.

If one accepts the arguments of Ross, molecular hydrogen should play no kinetic role in coal conversion. Elimination of hydrogen in favor of the polar solvent water should therefore enhance overall conversions. In this regard, we undertook four experiments, in the absence of molecular hydrogen, as illustrated in Table 3. Comparison of H_2O and D_2O with added KOH as a catalyst and tetralin as a solvent resulted in slightly lower conversions for the D_2O than H_2O experiments. More significantly, the conversions were considerably lower than those observed in Table 3 where less water, but molecular hydrogen was present. Clearly, molecular hydrogen plays a dominant role even when experimental conditions favor an ionic pathway. Since it is difficult to envision an ionic mechanism for the role of molecular hydrogen in liquefaction, such observations are inconsistent with a general ionic mechanism for

liquefaction and support the free radical hydrogenolysis mechanism proposed by Vernon (16).

Further evidence refuting not only an ionic mechanism, but the role of water as a reactant as well, can be found in comparison of Experiments 5B and 5C. Removal of the KOH catalyst and reduction of water by a factor of two resulted in no appreciable change in conversion.

A change in solvent from tetralin to SRC II, however, gave a dramatic decrease in conversion. Such an effect may be easily attributed to a lower number of hydrogen atom donors in SRC II when compared to tetralin. The significant role of such donors in water assisted liquefaction, regardless of the liquefaction mechanism, is clearly evident from these experiments.

2. MODEL COMPOUND STUDIES

In Appell's experiments with coal (13), the incorporation of deuterium into coal derived hydrocarbons, pyrene, and HHP was noted. Ross noted a lack of correlation between exchange and conversion in his study (14). Though his results suggested to Appell that water was a reactant under his conditions, these results could also be explained by an initial low temperature exchange of phenolic hydroxyls with D_2O, followed by higher temperature deuterium atom transfers between these now deuterated phenols and hydrocarbon radicals.

If our proposed explanation is operative, the use of O-alkylated coals could circumvent the low temperature exchange. Observation of deuterium exchange in coal products derived from such a coal may then indicate true reaction chemistry. Hydrolysis of the methyl ether of guaiacol by supercritical water was observed by Paulaitis, however. If the hydrolysis of methyl ethers is general and ionic in supercritical water, as their work with quaiacol would indicate, the formation of phenols from these hydrolysis reactions may also lead to exchange. Such an occurance would invalidate our arguments for the experiments with O-alkylated coal.

Further, the hydrogenolysis of anisole, as reported by Friedman (17), may also indicate a reaction pathway by which phenols, protected as methyl ethers, could react in what is essentially an exchange reaction. If the phenoxyl radical intially formed from anisole is reduced to the phenoxide ion, such exchange may occur. The observation of cresols in Friedman's work, however, would tend to indicate that such is not the case.

We attempted to address both concerns via the reaction of several model compounds with D_2O in the presence and absence of molecular hydrogen.

Significant exchange between bibenzyl and D_2O was observed only upon the introduction of molecular hydrogen to the system. Exchange was not observed with biphenyl either in the absence or presence of molecular hydrogen. These results suggest that H-atoms produced from the hydrogenolysis of bibenzyl reacted with the large molar excess of D_2O to produce HD and hydroxyl radicals. Once HD was formed, incorporation of deuterium into a variety of products would be expected. The hydroxyl radical could then capped by a variety of species, including molecular hydrogen in what would amount to a chain reaction.

There was no evidence for the observation of hydroxylated products in the total-ion-chromatograph (TIC) of the dichloromethane soluble fraction. The aqueous faction was unanalyzed.

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The TIC of the dichloromethane soluble products from the reaction of benzyl ethyl ether indicated only alcohol-d exchanged benzyl alcohol. There was no evidence in the mass spectra for incorporation of deuterium into any C-H bond. The hydrolysis appeared complete. It is important to note that molecular hydrogen was unemployed in this experiment.

Analysis of the TIC from the organic fraction of the similar reaction with dibenzyl ether indicated only unexchanged reactant. Benzyl alcohol was not observed.

Analysis of the dichloromethane soluble products from the reaction of 4-benzyl phenol with deuterium oxide in the absence of molecular hydrogen is most intriguing. Only 4-benzyl phenol was observed in the TIC, however, mass spectral analysis indicated the major product to be doubly labeled. Fragment ions clearly illustrate the incorporation of deuterium into C-H bonds.

Taken together, these results suggest electrophilic aromatic substitution between the actived phenol and a hydronium ion-d_3. Activation of the aromatic ring was insufficient with the other models to effect such exchange.

Additional experiments are currently underway in our laboratory to further substantiate this hypothesis. The possibility of similar reaction between coal and water would be easy to support. Coal would be expected to possess structural units with relatively low energy as carbocation leaving groups through substitution by a proton in water. Such moieties would include carbocations with the possibility of resonance stabilization by an aromatic system (e.g., benzyl carbocation), alpha to an ether oxygen (similar to those discussed by Larsen (18)) or carbonyls (e.g., decarboxylation).

Should additional model compound studies support the feasibility of similar reactions between water and coal, the observed enhanced yields from liquefaction with water may, at least partially, be attributed to the ipsosubstitution of a proton for a substituent on an aromatic moiety in coal.

This suggestion in no way presupposes that electrophilic aromatic substitution is the only mechanism operating in liquefaction. It may, however, indicate a dormant reaction pathway under the traditional donor solvent liquefaction conditions, which now contributes to the overall production of liquid products, thus the apparent increase in yield. The solvation effect of supercritical water in promoting these possibly new ionic pathways in aqueous liquefaction is currently under investigation in our laboratory.

ACKNOWLEDGEMENTS

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TABLE 1. ELEMENTAL ANALYSES OF COAL AND VEHICLES.[a]

Material	C	H	N	O	S
Illinois No. 6 Coal, River King Mine[b]	73.7	5.6	1.5	14.8	4.5
SRC-II Distillate	87.1	8.0	1.4	3.0	0.4

[a] wt.%, daf basis, Huffman Labs, Wheatridge, Colo.

[b] Moisture-free ash content was determined to be 13.6 wt.% for the River King Coal. As used, the coal contained 3 wt.% water.

Table 2. Comparison of H_2O and D_2O as Vehicles Under Water Assisted Liquefaction Conditions[1]

Ex. #	Vehicle	Conversion[2]
4A	H_2O	68
4B	D_2O	70

[1] Reaction Conditions: 4.00 g River King Coal; 1.70 g H_2O or D_2O; 1.50 g tetralin; 1200 psig H_2 (cold); 385°C; 20 mins. at temp.; 2 mmol Cs_2CO_3 added via the water.

[2] DAF basis; average of duplicate runs; reproducibility ± 1 wt. %.

Table 3. Aqueous Liquefaction Without Molecular Hydrogen[1]

Ex.#	Vehicle	Solvent[2]	Catalyst[3]	Est. Reaction[4] Pressure	Water[5] Density	THF Conversion[6]
5A	D_2O (22 mmol)	Tetralin	KOH (8 mmol)	4350	0.110	42
5B	H_2O (22 mmol)	Tetralin	KOH (8 mmol)	4350	0.097	45
5C	H_2O (9 mmol)	Tetralin	-----------	1790	0.043	46
5D	H_2O (9 mmol)	SRC II	-----------	1790	0.043	26

1 Reaction Conditions: 4.00 g River King Coal; 385° C; 40 minutes at temperature

2 1.50 g per reactor

3 as an aqueous solution

4 as calculated by van der Waal's Equation does not include solvent contributions

5 g/cc

6 DAF basis; average of duplicate runs; reproducibility ± 1 wt. %

REACTIONS OF LOW-RANK COALS IN SUPERCRITICAL METHANOL

Edwin S. Olson, Michael L. Swanson, Steven H. Olson and John W. Diehl

University of North Dakota Energy Research Center
Box 8213, University Station
Grand Forks, North Dakota 58202

Supercritical fluid extraction of coals has been investigated as a promising method for the production of liquid fuel products from coal under mild conditions. Studies with alcohols as the supercritical fluid have recently been reported (1, 2, 3, 4). Alcohols would be expected to exhibit greater solubility for polar organic molecules, because of hydrogen bonding or dipole attractive forces; they also provide the opportunity for chemical reactions during the extraction, because of the nucleophilicity of the alcohol oxygen and the tendency to act as a hydrogen donor. Alkylation reactions can also occur. Chen and coworkers have shown that sulfur compounds were removed selectively in supercritical methanol and ethanol extractions (4). This potentially useful application may involve reaction of the alcohol with some of the organosulfur moieties and possibly pyrite in the coal. The exact mechanism of the sulfur removal reaction is unknown. Earlier workers used alcohols at very high temperatures (460-600°C) (5) or in combination with sodium hydroxide (6).

As a part of our study of the interaction of supercritical solvents with low-rank coals, a series of extractions of lignites and subbituminous coals were performed with supercritical methanol in a semicontinuous extraction apparatus. These studies were concerned with establishing yield and conversion data for several coals at various supercritical conditions. Not only can the solvation power of the solvent (which depends on the fluid density) be conveniently controlled over a large range with changes in solvent pressure or temperature, but the rates of chemical reactions occurring in and with the solvent may also be controlled by the wide variation in viscosity and density which are obtained with supercritical fluids.

Experimental

Supercritical methanol extractions were performed using the semicontinuous processing unit described earlier (7). Methanol solvent was pumped through the fixed coal bed (50 g of dried coal) at 120 ml/hr for 2 hr. The pressure of the supercritical solvent was reduced to atmospheric pressure after passing a back pressure regulator. The extract and solvent were collected in a chilled sample vessel. The noncondensable product gas was measured and collected for subsequent GC analysis. Both the solvent-extract mixture and the extracted coal residue were rotary vacuum distilled to give a moisture and methanol free product. Extracts were analyzed by a number of methods including extraction into base, HPLC and ^{1}H-NMR of methylated (diazomethane) samples and GC for quantitative determination of individual phenols and carboxylic acids. The phenol analysis involved addition of 2-fluorophenol as an internal standard, extraction into base to remove hydrocarbons and anisoles, addition of acid and extraction into chloroform, Kuderna-Danish evaporation of the chloroform and GC analysis on a calibrated 60 m DB5 capillary column (FID). Photoacoustic spectra of the coal residues were obtained using a cell obtained from MTech Photoacoustics with a Nicolet 20SXB spectrometer. Thermogravimetric analyses of the coal residues were obtained using a Cahn 2000 thermobalance with an argon atmosphere and a 20°C/min temperature ramp.

Results and Discussion

Effects of Temperature and Pressure on Yields

Table 1 summarizes the operating conditions and the experimental results obtained for the supercritical methanol extractions. A series of runs at 250 C using Indian Head lignite was performed at pressures ranging from 1233 psia to 2935 psia (P_r = 1.05 to 2.5). The conversions (weight loss on a maf basis) were found to increase with increasing pressure (i.e. from 4.3 to 6.1 %), while the extract yields (weight of extracted material recovered on an maf basis) increased from 1.8 to 4.4% respectively. This increase in extract yields with pressure can be attributed to change in solvent density. Figure 1 is a plot of the effect of calculated solvent density on the extract yields from Indian Head lignite.

A series of isobaric experiments were performed at 2348 psia (P_r = 2.0) with temperatures at 250, 275, 300 and 350°C using several coals. The conversion and extract yields all increased significantly with temperature, however, at the higher temperatures the extract and gas yields become significantly higher than the actual weight loss of the original coal. This net yield of products suggests that the methanol is being incorporated into the products by reacting with various groups in the coal and extract components and also being converted to gas, which contains large amounts of methane.

Table 1. Operating Conditions and Results from the Extraction of Various Coals with Supercritical Methanol. See Table 3 for coal analyses. Reduced temperature (Tr) and reduced pressure (Pr) are the ratios of temperature and pressure to supercritical temperature and pressure.

Coal	Temp. (°C)	Tr	Pressure (psia)	Pr	Calc. Solvent Density (g/ml)	Pct. Conv. (maf)	Pct Yield, maf Extract	Gas
Indian Head	250	1.021	1233	1.050	0.134	4.27	1.76	2.25
Indian Head	250	1.021	1468	1.250	0.295	4.98	2.86	2.05
Indian Head	250	1.021	1761	1.500	0.368	4.17	3.05	1.36
Indian Head	250	1.021	2348	2.000	0.412	5.49	3.80	1.66
Indian Head	250	1.021	2935	2.500	0.434	6.13	4.43	2.23
Indian Head	275	1.069	2348	2.000	0.320	8.20	3.88	3.67
Indian Head	300	1.118	2348	2.000	0.224	9.55	4.74	6.91
Indian Head	350	1.216	2348	2.000	0.144	23.30	12.43	22.04
Wyodak	250	1.021	1233	1.050	0.134	1.56	3.08	0.70
Wyodak	250	1.021	2348	2.000	0.412	4.16	6.33	0.65
Wyodak	300	1.118	1233	1.050	0.079	2.73	11.28	3.49
Wyodak	300	1.118	2348	2.000	0.224	6.17	6.59	3.10
Wyodak	350	1.216	1233	1.050	0.063	14.74	12.39	21.60
Wyodak	350	1.216	2348	2.000	0.144	17.55	23.29	22.61
Deer Creek	250	1.021	1233	1.050	0.134	0.20	4.02	0.37
Deer Creek	250	1.021	2348	2.000	0.412	10.11	10.50	0.16
Deer Creek	300	1.118	2348	2.000	0.224	7.99	8.69	0.75
Deer Creek	350	1.216	2348	2.000	0.144	11.79	13.69	5.17
Martin Lake	250	1.021	2348	2.000	0.412	3.95	5.57	0.69
Martin Lake	300	1.118	2348	2.000	0.224	5.60	6.64	1.93
Martin Lake	350	1.216	2348	2.000	0.144	18.24	17.54	19.88

Composition of the Extracted Material

The composition of the extract obtained from each of the coals varied substantially with the increase in temperature of the extraction with supercritical methanol. The extracts contained the waxy material (alkanes and long chain fatty acids) which were also present in the hydrocarbon extracts of the these coals (7). In addition, the methanol extractions contained phenolics, anisoles and methyl esters of mono and dicarboxylic acids. The phenolics and anisoles predominate in the extractions of Indian Head lignite which were carried out at the higher temperatures (Table 2). The methyl esters of dicarboxylic acids, such as dimethyl succinate, predominate at the lower temperature. The anisoles and methyl esters have not been found in any supercritical hydrocarbon solvent or water extraction products from coal nor in any pyrolysis products. The anisoles resulted from methylation of the corresponding phenol hydroxyl groups. The esters have resulted from esterification of carboxylic acids in the supercritical methanol; however, the dicarboxylic acids required for these reactions are produced from the coal by oxidation rather than pyrolysis. Thus the reactions for formation of esters have not been sufficiently elucidated.

Table 2. Yields of Phenols in Supercritical Methanol Extractions as Wt% of Extract Weight.

	Indian Head Lignite (1)			Wyodak Subbituminous			
Phenol	250	300	350	250 (1)	300 (1)	350 (1)	350 (2)
Phenol	.18	.44	.77	.059	.056	.066	.038
o-Cresol	.01	.36	2.02	.007	.065	.149	.132
m-Cresol	.03	.33	1.25	.024	.080	.056	.060
p-Cresol	t	.47	.45	.032	.037	.045	.030
Guaiacol	.42	1.17	1.30	t	t	.003	t
2,6-DiMePhe	t	.19	3.86	.003	.041	.435	.388
2-EtPhe	0	.05	0.43	.003	.014	.019	.022
2,4-DiMePhe	t	.41	5.57	.005	.123	.178	.199
2,5-DiMePhe	t	.04	.97	.002	.020	.041	.055
2,3-DiMePhe	.02	.32	2.37	.006	.045	.117	.116
4-MeGuaicol	.10	.82	1.98	t	t	.035	.030
2,4,6-TriMePhe	t	.29	13.22	.001	.070	.549	.571
2,3,6-TriMePhe	t	.08	3.61	t	.024	.211	.311
4-MeOPhe	0	.01	.43	t	t	.004	.012
2,4,5-TriMePhe	t	.04	4.42	.007	.040	.092	.114
4,6-DiMeGua	t	.41	1.86	t	t	.045	.004
4-Indanol	t	.24	1.77	.003	.081	.099	.127
3,4,5-TriMePhe	t	t	.84	0	0	.004	.003
5-Indanol	t	.03	.57	.001	.014	.024	.032
2,3,5,6-TMePhe	t	.07	5.59	.003	.016	.147	.252
4-nPrGuaiacol	.02	.22	.58	0	0	.002	.009
1-Naphthol	t	.02	.28	.006	.002	.001	.003
2-Naphthol	t	.05	1.40	t	t	.019	.001

Pressures: (1) = 2348 psia; (2) = 1233 psia

Abbreviations: Phe = phenol; Me = methyl; Et = ethyl; Pr = propyl; Gua = guaiacol; MeO = methoxy; T = tetra; t = trace

Other phenols identified by GC/MS and retention time but not quantitatively determined: 6-MeGuaiacol, 3,4-DiMePhe, 3,5-DiMePhe, 4-EtPhe, 4-EtGuaiacol, 2,3,5-TriMePhe, 2,3,4,6-TMePhe, EtMePhe (5).

The distribution of phenol types found in the extracts of Indian Head lignite carried out at 250° (Table 2) was similar to that found in pyrolysis products (8); that is, large amounts of phenol and cresols, smaller amounts of virtually every type of alkyl phenol isomer, a limited series of mainly 4-substituted guaiacols and catechols (these were not quantitatively analyzed). Since the Wyodak subbituminous coal has a very small methoxy group content, corresponding to a low concentration of guaiacol groups in the coal, only traces of guaiacols were found in the low-temperature extracts. The yields of phenols from the Indian Head extractions were much higher than those from the Wyodak coal at all temperatures.

With both coals the higher temperature extractions yielded a distribution of phenols distictly different from that obtained in the low-temperature extractions. Large increases in the yields of 2,6-dimethylphenol and 2,4,6-trimethyl phenol were especially noticeable. This is evidence for methylation of the ring carbons of the phenols which occurs mainly at the positions ortho to the hydroxyl group of the phenol. In addition to the quantities reported in Table 2 for the phenols which were included in our calibration, numerous other C_4-, C_5- and C_6-substituted phenols were identified in the 350° extracts by GC/MS. Methylation of the aromatic rings of the guaiacols and catechols was also observed to have occurred during the extraction at high temperatures; large amounts of 4,6-dimethylguaiacol, 3,4-dimethylguaiacol, 3,6-dimethylguaiacol, C_3-guaiacols, C_4-guaiacols and C_5-guaiacols were found by GC/MS. Most of the components of the product from extraction of Indian Head lignite at 250°C and most of the low molecular weight products from extraction at higher temperatures have been identified; however, many of the Wyodak extraction products are still under investigation.

The effects of pressure on the yields of phenols was investigated at two pressures, 2348 psia and 1233 psia. The data for extraction of Wyodak subbituminous coal at 350°C at these two pressures are presented in Table 2. Similar yields for each of the individual phenols are observed. The phenol yield structure is therefore dominated by temperature rather than pressure effects, consistent with the hypothesis that release of phenols from the coal matrix is controlled by activation energies for bond cleavage rather than diffusion. Density and viscosity effects on the phenol reaction products are negligible.

Comparison of residue surface groups

The residues from the supercritical methanol extraction of Indian Head lignite at three temperatures were examined using photoacoustic spectroscopy to determine the changes in functional groups on the surface which result from extraction and reactions of the lignite with the solvent. The spectra for the original dried lignite and three residues are shown in Figure 2. The broad carboxyl OH stretching band extending from 3500 to 2000 cm^{-1} progressively decreases with samples of increasing extraction temperatures, corresponding to conversion of the carboxylic acids to methyl esters or to decarboxylation. The carbonyl stretching band in the original lignite at 1695 cm^{-1} is changed to 1717 cm^{-1} (with shoulder at higher wave number) in the 250° and 300°C extracts, also indicating the conversion to the ester. The carbonyl band decreases somewhat and exhibits a peak at 1730 cm^{-1} in the 350°C extract, which indicates further conversions. The intensities of the methyl absorptions at 2960 and 1455 cm^{-1} increase significantly with the extraction temperature. These changes in vibrational bands of the surface groups are consistent with the alkylation which has occurred during the extraction with supercritical methanol.

Thermogravimetric data obtained with the extracted coal residues indicate that the supercritical methanol extracts a significant portion of the compounds which would have normally volatilized in the 200° to 400°C range. These curves also exhibit the effect of methylation of oxygen groups which thermally decompose at temperatures above 400° resulting in release of additional products.

Table 3. Proximate and Ultimate Analyses of Coal Samples Used in Experiments.

	Wyodak	Deer Creek	Gascoyne	Indian Head	Martin Lake
Proximate Analysis					
Volatile Matter	43.5	42.0	40.1	43.8	42.2
Fixed Carbon (by diff)	50.0	47.2	41.2	48.0	42.8
Ash	6.5	10.8	18.6	8.5	15.0
Ultimate Analysis					
Hydrogen	4.26	5.66	3.93	4.74	0.32
Carbon	64.62	71.21	57.56	66.20	61.88
Nitrogen	1.01	1.27	.87	.96	1.23
Sulfur	.58	.36	1.76	.72	1.17
Oxygen (by diff)	23.04	10.70	17.28	19.19	20.40
Ash	6.5	10.8	18.6	8.2	15.0

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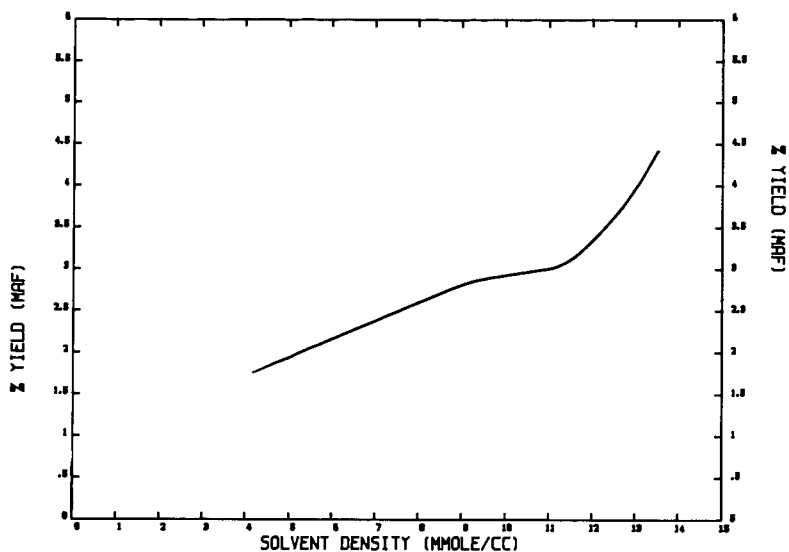
Figure 1. Plot of extraction yields from Indian Head lignite versus solvent density of methanol at 250°C.
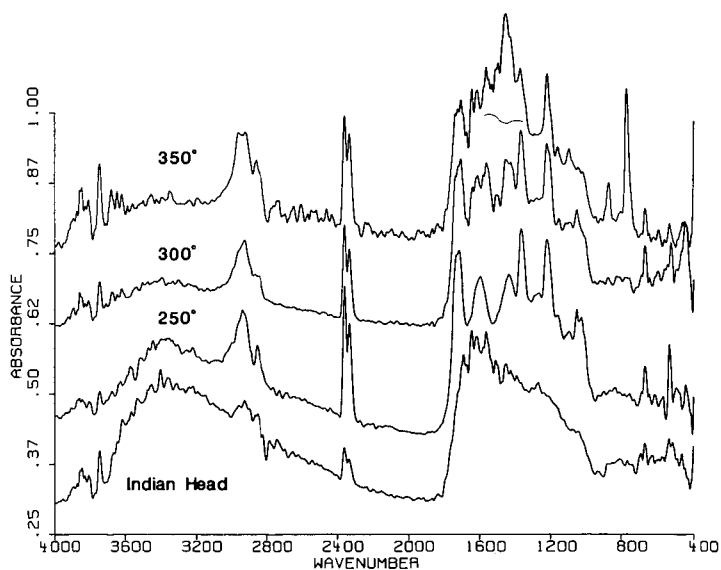

Figure 2. Photoacoustic spectra of dried Indian Head coal and residues from supercritical methanol extraction.

THE CHEMCOAL PROCESS
FOR
LOW TEMPERATURE CONVERSION

C.R. Porter[1], C.L. Knudson, Ph.D.[2], and J.R. Rindt[2]

[1]Carbon Resources, Inc.
4892 Independence St., Suite 130
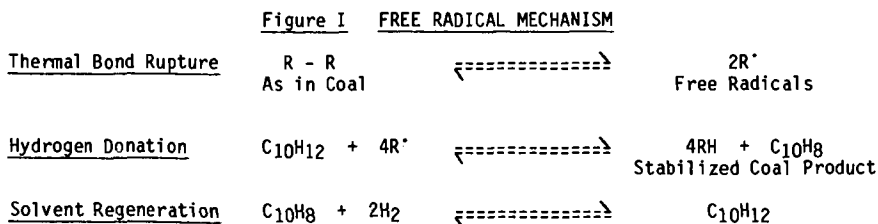Wheat Ridge, Colorado 80033

[2]University of North Dakota Energy Research Center
Box 8213
University Station
Grand Forks, North Dakota 58202

INTRODUCTION

The ChemCoal Process utilizes chemical means to transform coal and other carbonaceous materials to solid, liquid, and slurry products. The process uses coal-derived solvents and aqueous alkali to dissolve and breakdown carbonaceous materials. Carbon monoxide is used to generate hydrogen via the water gas shift reaction to cap organic species. Insoluble sulfur and ash impurities are separated from the soluble organic fraction. Recycle solvent, light oils, alkali, and water are extracted from the soluble fraction and preasphaltenes (PA) and asphaltenes (A) are precipitated by the addition of methanol. The precipitated PA and A, the ChemCoal solid products, have been slurried and used in a diesel engine. The methanol fraction is processed to recovery recycle solvent, alkali, water, light oils, and methanol. The process has been evaluated under continuous process operation at the University of North Dakota Energy Research Center (UNDERC). A 10 TPD demonstration plant is proposed and will be sited near Powhatan Point, Ohio.

CLASSICAL THERMAL PROCESSES

Classical direct coal liquefaction processes involve high temperature thermal treatment of coal to rupture chemical bonds producing free radical coal fragments. The free radical fragments are stablized by capping with hydrogen of a coal-derived solvent usually represented as Tetrahydrodecalin (THD), $C_{10}H_{12}$. This is represented as Figure I.

Figure I   FREE RADICAL MECHANISM

Thermal Bond Rupture	$R - R$ As in Coal	$\rightleftharpoons$	$2R^{\cdot}$ Free Radicals
Hydrogen Donation	$C_{10}H_{12} + 4R^{\cdot}$	$\rightleftharpoons$	$4RH + C_{10}H_8$ Stabilized Coal Product
Solvent Regeneration	$C_{10}H_8 + 2H_2$	$\rightleftharpoons$	$C_{10}H_{12}$

The classical process requires tempertures and pressures of approximately 425°C and 2500 psig. In the SRC process thermal bond rupture, hydrogen donation and solvent regeneration are carried out simultaneously in the liquefaction reactor. The hydrogen gas treatment rate may be 20,000 SCF/ton of coal feed with a consumption of 4,000 SCF/ton of coal.

Competing free radical reactions, not shown in Figure I, can occur resulting in recondensation of the free radical coal fragments and degradation of the hydrogen shuttle species. Hydrogen shuttle species are converted to degradation spe-

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cies which do not lend themselves to regeneration. Conditions which favor the hydrogen donation reaction do not necessarily favor solvent regeneration. The EDS process attempts to overcome the solvent degradation and regeneration limitations by use of a separate catalytic regeneration reactor.

IONICALLY-AIDED CONVERSION

The chemical transformation of coal, by the ChemCoal Process, may make use of ionic chemistry while benefiting from low temperature thermal bond rupture mechanisms. Ionic reactions are represented in Figure II.

ChemCoal Process mechanisms may benefit from both ionic and thermal processes. The keto form of the o-(hydroxyphenyl)phenylmethane, OPPM, shown in Figure II is more easily formed into toluene and phenol than the enol form. The C-C bond shown by 'x' in II decreases in strength from 86 to 46 kcal/mol. This decrease in bond strength, due to a shift from sp^2-sp^3 to sp^3-sp^3 bondings as well as its allylic position with respect to the oxygen atom, is correlated to a decrease in activation energy over unassisted bond cleavage. The major effect of a nucleophile such as PhO^- is to facilitate proton transfer in keto/enol tautomerisms. The bond may then be broken homolytically at a lower temperature. Keto-enol tautomerisms may be ionically aided leading to the low temperature thermal bond rupture.

The role of the PhO^- and formate mechanism in the ChemCoal Process has been reported by Porter and co-workers.[1] The role of oxygenates on hydrocarbon bond dissociation has been reported by McMillen and co-workers.[2][3][4]

In the ChemCoal Process the transformation of coal is achieved at about 325°C and 1250 psig in the presence of phenolics, added alkali and water, and carbon monoxide. The requirement for tetralin or other hydrogen shuttles does not exist. Hydrogen plays a part in the conversion but an external source of hydrogen is not required, as the hydrogen is supplied from the water and CO.

Under the ChemCoal processing conditions, the water gas shift reaction (WGSR) is promoted. It has been observed in the laboratory that those conditions which promote the WGSR do not necessarily promote transformation of coal. Therefore, it is assumed that there is a competing reaction but the presence of hydrogen and the formate ion are beneficial.

FIGURE II. THERMAL BOND RUPTURE AND ISOMERIZATION OR H—CAPPING IN THE PRESENCE OF A SUITABLE H—DONOR

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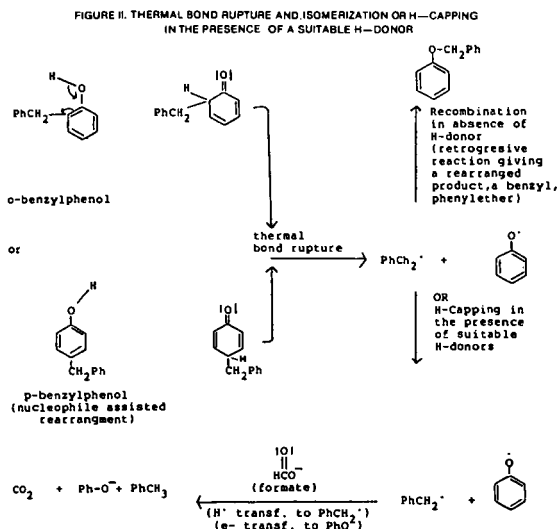
PROCESS DESCRIPTION

The ChemCoal Process involves the following five steps shown in Figure III:

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                    │
                    ▼
          ┌───────────────────┐              
          │    Preparation    │◄─────────────────┐
          └───────────────────┘                  │
                    │                             │
                    ▼                             │
   CO     ┌───────────────────┐                  │
   ───────►│    Solvation     │                  │
          └───────────────────┘                  │
                    │                             │
                    ▼                             │
          ┌───────────────────┐                  │
          │      Solid        │                  │
          │    Separation     │                  │
          └───────────────────┘                  │
                    │                             │
                    ▼          CH3OH             │
          ┌───────────────┐   ◄──── ┌────────────────┐
          │    Liquid     │         │  Distillation  │
          │  Extraction   │ ──────► └────────────────┘
          └───────────────┘                  │
                    │                         │
                    ▼                         ▼
            ChemCoal Solid              Distillates
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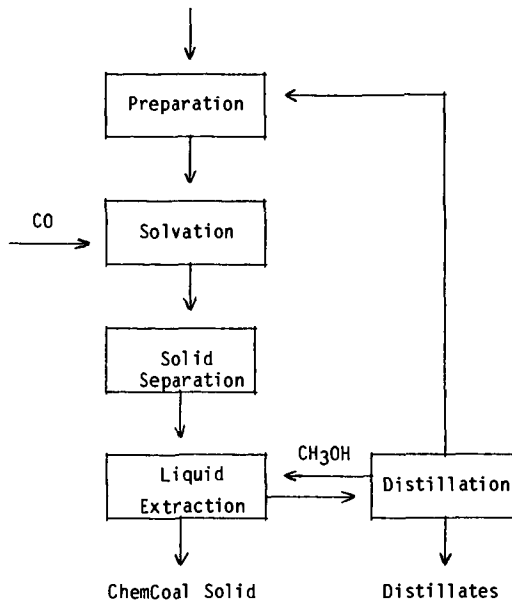
Preparation:	The coal is crushed and mixed with recycle solvent.
Solvation:	The coal slurry is heated to about 325°C in the presence of syngas at approximately 1250 psig. The preheater and reactor design incorporates a slow heating rate and a means to maintain S/C ratios in the reactor.
Solid Separation:	The slurry is centrifuged to remove the solids.
Liquid Separation:	The filtrate is treated with methanol to extract phenol, water, and alkali. The ChemCoal solid precipitates and is separated from the liquid phase.
Distillation:	The liquid phase is distilled to recover methanol, distillates, and recycle solvents.

PROCESS RESULTS

Table I summarizes the ultimate analysis of three ChemCoal Process coal-derived solid products. It is important to note that the coal-derived products are similar to No. 2 and No. 6 fuel oil in terms of sulfur, nitrogen, and ash content.

Table I   ChemCoal Product Analyses Compared to Fuel Oils

Coal Rank:	Lignite	Bituminous	Fuel Oil	Fuel Oil
Source:	No. Dak.	Ohio No. 6	No. 6	No. 2
Ash	0.19	0.12	0.01- 0.5	Nil
Carbon	83.5	86.06	86.5 -90.2	86.1-88.2
Hydrogen	6.41	6.11	9.5-12.0	11.8-13.9
Nitrogen	0.92	1.23	2.0	0.2
Sulfur	0.25	0.41	0.7- 3.5	.05- 1.0
Oxygen (diff)	8.73	6.07	2.0	Nil
HHV (Btu/lb)	15,400	15,700	17,400-19,000	19,000-19,750
lb Ash/MMBtu	0.115	0.076	0.005-0.30	Nil
lb SO_2/MMBtu	0.32	0.52	0.75-4.0	05.1.0

Other ChemCoal Product Properties (typical):
   Autoignition Temperature 1100, ± 30°F
   Equilibrium Moisture 0.9%
   Specific Gravity 1.03

    Also of concern in the processing of coal is the sulfur and ash content of the products. Results obtained from a series of coals are summarized in Table II which shows that the products are very low in ash and sulfur content. In the case of an Eastern coal from the Sunnyhill Mine in Ohio (Ohio No. 6 seam), it is seen that the sulfur and ash content are reduced from 2.11 weight % to 0.41 weight % and 10.5 weight % to 0.12 weight %, respectively. In the case of the Western low-rank coal from the Indian Head Mine (Zap seam) of North Dakota, the sulfur and ash are reduced from 1.18 weight % to 0.25 weight % and 12.93 weight % to 0.19%, respectively.

Table II   ChemCoal Process Results

Feedstock:	Coal Feed[a]		ChemCoal Product[a]		Percent Reduction	
Identification:	Sulfur	Ash	Sulfur	Ash	Sulfur	Ash
Ohio No. 6 (Sunnyhill)	2.11	10.5	0.41	0.12	80.6	98.9
North Dakota Lignite (Indian Head Mine)	1.18	12.93	0.25	0.19	78.8	98.1
Colorado Wadge (Energy Fuels II)	0.51	8.56	0.23	0.03	54.9	99.6
Texas Lignite (Big Brown)	0.85	14.10	0.07	0.07	91.8	99.5

[a] Weight percent, on a moisture-free basis.

CONTINUOUS PROCESS UNIT (CPU) OPERATION

    A continous process unit was operated at UNDERC under the ChemCoal processing mode. The unit is depicted schematically in Figure IV[5]. Table III summarizes the operating conditions for the CPU test on an Indian Head Lignite. The CPU operated for 40 recycle passes. During passes 30-39, GC/MS data indicated the recycle solvent was approximately 95% coal-derived from the process.
    Table IV summarizes the results from the recycle test. The results confirmed earlier batch conversion data, established operability of the process, and solvent balances.

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FIGURE IV
The ChemCoal CPU Scheme

FIGURE 2.4. Developing Stream Data as wt% of Feed Slurry

Table III   ChemCoal Recycle Test - Operating Conditions

Indian Head Lignite

- 1.8 solvent-to-coal ratio (2.5 lbs/hr)
- Alkali at 6% of MAF coal
- Preheater/reflux -- 250°C/1800 psi
- Reactor/reflux -- 340°/1800 psi
- Syngas feed before reactors (7 SCFH)
- MEOH addition to PPT ChemCoal solids
- Centrifuge -- solids removal
- Distillation -- 19" VAC/100°C

Table IV   ChemCoal Recycle Test - Results

Indian Head Lignite

- System operable for 40 recycle passes
- Solvent balance achieved
- Conversions -- ≃ 85% MAF coal
- Reductant consumption (CO) in H_2 equivalents ≃ 1.5% MAF coal
- Gas make -- ≃ 2.0% MAF coal
- PA and A yield -- 50% MAF coal
- Distillate yield -- 30% MAF coal

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CHEMCOAL ASSOCIATES
CONCEPTUAL PROCESS DEMONSTRATION
FLOW DIAGRAM
FIGURE V

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DEMONSTRATION PLANT

An overall block flow diagram of a conceptual 10 TPD ChemCoal demonstration plant is shown in Figure V. A brief description of the processing steps is given in the following paragraphs.

The coal is received from storage, crushed and ground to 80% minus 200 mesh. The coal is then mixed with two parts of process-derived recycle solvent to one part coal and an amount of aqueous alkali.

The slurry mix is pumped to about 1500 psig through a heater/preheater/reactor system. In the presence of carbon monoxide, coal solvation occurs at about 340°C.

The reactor effluent mixture (gas, liquid, and solids) is separated in a phase separator. Residual liquids are condensed from the gas stream and returned to the liquid slurry streams. The gases are flared and scrubbed to remove noxious species.

The slurry stream is processed through a centrifuge to remove solids. The filter cake (centrifuge solids) is washed to recover process solvent constitutents, which are returned to the process. The cleaned cake is rendered inert by heat treatment (pyrolyzed), all liquids returned to the process, and all gases (not shown) flared and scrubbed.

The filtrate (centrifuge liquids) are contacted with a recycle methanol stream. The ChemCoal solid product (coal-derived preasphaltenes and alphaltenes) precipitates when contacted with methanol. The precipitate is removed by centrifugation, washed, and stored for subsequent product testing. The liquid stream is distilled to recover recycle solvent, coal-derived distillate, and methanol.

ChemCoal Associates, a joint teaming arrangement between Carbon Resources, Inc., CRI Associates, Limited, and The North American Coal Corporation is planning to design, construct, and operate a demonstration plant at a facility near Powhatan Point, Ohio. The University of North Dakota Energy Research Center and the MK-Ferguson Company of Clevland, Ohio are assisting ChemCoal Associates in this effort.

ACKNOWLEDGEMENTS

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THE DIRECT USE OF NATURAL GAS IN COAL LIQUEFACTION

Muthu S. Sundaram* and Meyer Steinberg
Process Sciences Division
Brookhaven National Laboratory
Upton, New York 11973

The main objective in coal liquefaction is to convert coal into a better fuel that is easier to transport and cleaner to burn. During the liquefaction process, the macromolecular network of coal substance is broken into smaller units and rearranged into lighter products of reduced molecular weight. More specifically, the chemical conversion of coal involves an upgrading in its hydrogen content or in other words, increasing the H/C ratio.

In liquefaction, this is achieved by rapidly heating coal, slurried in a hydrogen donor vehicle, to temperatures of 350-500°C for considerably long residence times. The slurry vehicle serves both as a dispersant as well as the reactant. The commonly employed slurry vehicles contain partly saturated structures such as tetralin. The importance of the vehicle was recognized by Fischer in 1937[1] and the role of hydrogen transfer from vehicles to coal was discussed by Curran et al.[2] Recently Neavel studied the hydrogen transfer process in much more detail.[3,4] In these interesting studies, he found that during initial stages of liquefaction, very little hydrogen is required to stabilize the free radicals generated from coal; however, during the later stages - when more benzene-soluble products are formed - each successive increment of benzene-soluble material required more hydrogen than the previous increment. For example, the incremental conversion from 40 to 50% consumed 0.23 parts by weight of hydrogen, whereas the same 10% conversion increment from 80 to 90% consumed 0.8 parts by weight of hydrogen. Thus, the hydrogen transfer and hence hydrogen requirement is found to increase exponentially with coal conversion.

The hydrogen required has to come either from the coal itself or it must be supplied from an external source, e.g. the slurry vehicle or gaseous hydrogen, or both. A large number of solvents have been used as slurry vehicles. The hydrogen donor capacity of a solvent depends on its molecular structure. Wise found that the hydro-aromatic compounds were more effective hydrogen donors than the aromatic analog; for example, piperidine/pyridine, pyrolidine/pyrrole, indoline/indole, tetrahydroquinoline/quinoline, tetrahydronaphthalene (tetralin)/naphthalene, perhydropyrene/pyrene, etc.[5] Tetralin has been used as a hydrogen donor solvent for a long time.[6] The use of synthetic recycle solvents has increased recently for economic process purposes. However, for laboratory research studies, tetralin is still used extensively where a hydro-aromatic solvent is required.

The hydro-aromatic solvents, rich in donor hydrogen, can meet the hydrogen demand even in the absence of gaseous hydrogen. However, in most of the processes currently under development, solvents with high hydro-aromatic contents are not always practical. For example, in the Exxon donor solvent (EDS) process, in which an externally hydrogenated recycle donor solvent is used, about 50% of the hydrogen requirement is directly

met by the gaseous hydrogen.[7,8] Thus, if the concentration of hydro-
aromatics is less in the recycle solvent, then the gaseous hydrogen would
be anticipated to make up the deficiency. This was the case in which an
Illinois No. 6 (Monterey) coal was reacted for 90 minutes under 1000 psi
hydrogen pressure in the presence of synthetic recycle solvents of varying
tetralin contents.[9]

Vernon[10] studied the role of molecular hydrogen on the pyrolysis
of model compounds present in coal. From this study, he concluded that,
"...high pressure hydrogen can promote the hydrocracking of some carbon-
carbon bonds in the coal structure that are too strong to break thermally,
and lead to higher distillable liquid yields." This is also supported by
the SRC-I Pilot Plant data.[11] An increase in the partial pressure of
hydrogen in the dissolver increased the coal conversion with an attendant
increase in the hydrogen consumption. In short-contact-time-liquefaction
of several coals of different ranks, the low rank coals consumed greater
amounts of hydrogen than the high rank coals and in those cases where the
hydrogen consumption was high, substantial quantity of hydrogen was derived
from the hydrogen gas.[12] Under long residence times, the hydrogen con-
sumption increased monotonically, both with temperature and pressure.[13]

The deuterium tracer method developed by Heredy and coworkers has re-
vealed that the hydrogen contact opportunity is very important for the pro-
duction of soluble products. The soluble products increased from 3 to 11
to 23%, as a result of increasing the hydrogen contact opportunity. They
concluded that apparently there was a direct route for incorporation of de-
uterium (presumably hydrogen, too) into the coal matrix without the aid of
tetralin.[14,15]

Recent studies by Morita, et al[16] show that the effect of hydro-
gen pressure on coal hydrogenation was influenced by the type of coal used.
The liquefaction conversion of a low volatile, oxygen rich Morwell coal
(Australia) was not affected by hydrogen pressure. On the other hand, high
oil yields were obtained from a high volatile Taiheiyo coal (Japan) at high
hydrogen pressures.

Wilson, et al[17] have concluded that the large consumption of
hydrogen at 400-425°C and 1000 psi hydrogen pressure, in tetralin donor
solvent liquefaction of Australian Liddell coal, is not due to the hydro-
genation of the aromatic ring, but due to the alkyl bond fission and hy-
drogenolysis reactions. Thus, high hydrogen pressures can lead to enhanced
yield of by-product hydrocarbon gases, C_1-C_4, which result in the unprofit-
able consumption of expensive hydrogen.

It appears that certain constituents of coal mineral matter may have
catalytic effect on the hydrogen transfer. The general agreement is that
iron containing minerals, Fe_2O_3 and iron sulfides in particular, are ex-
ceptionally good in enhancing the distillable product yield.[18,19]

All existing processes for direct liquefaction of coal by solvent extraction, SRC-I, SRC-II and SRC-SCTL processes, the EDS process and the H-coal process, utilize molecular hydrogen at high pressures (over 1000 psig). The total hydrogen consumption is in the range of 3-5% of the amount of the coal feed of which a significant portion comes from molecular hydrogen depending on the rank of the coal and the quality of the recycle oil. The cost analysis of a typical coal liquefaction process shows that as much as one-third of the overall cost goes towards hydrogen production.[20]

This, naturally, has increased interest in finding cheaper substitutes for expensive hydrogen. The use of CO, $CO-H_2O$ and $CO-H_2$ in direct coal liquefaction has been explored.[21-24] The beneficial effects of direct addition of H_2S on coal liquefaction has also been reported by several workers.[25,26] More recently, addition of H_2S to the synthesis gas in the liquefaction of a lignite has been found to increase the hydrogen donor capacity of the recycle solvent.[27] The catalytic activity of sulfide minerals in coal liquefaction largely seems to be related to the capacity to generate H_2S via free radical chain reactions.[28,29] However, H_2S might be advantageously recycled only in a process where a high degree of sulfur removal is not required. This is due to the decreased sulfur removal from the product despite the improved conversion of coal. For example, increasing the partial pressure of H_2S, from 6 psi to 40 psi in 1600 psi hydrogen, caused a decrease in the THF insolubles from 10.4 to 5.6%, but at the same time the sulfur in the product liquid rose from 0.45 to 0.61%.[30] This can impose a severe economic penalty.

One of the reasons for the use of $CO + H_2$, $CO + H_2O$, $CO + H_2 + H_2S$, and H_2S in coal hydrogenation is that these gases are produced during the coal liquefaction, and in a real process they could be recycled. It is noted, however, that among the gaseous reaction products, the yield of light hydrocarbon gases (C_1 to C_4), in general, is greater than the combined yield of gases containing hetero-atoms. Roughly, about half of the C_1-C_4 light hydrocarbons is made up of methane alone and the low rank coals produce far greater amounts of methane and C_2-C_4 gases than the higher rank coals.[31]

This leads to an interesting possibility of using methane as a substitute for hydrogen in the direct liquefaction of coal. Though methane gas is homogeneously stable at liquefaction temperatures (methane is thermodynamically stable to temperatures of 750°C), thermally produced free radicals from coal and, the free radicals from the solvent can abstract hydrogen atom from methane, thereby setting the stage for an array of free radical reactions. It should be noted that methane and hydrogen both have the same bond dissociation energy ($CH_4 \longrightarrow CH_3\cdot + H\cdot$ and $\longrightarrow$ H_2 H. + H.) equal to 104 Kcal/mole.[32] It is possible that during the course of the free radical reactions, the methyl radicals generated from the dissociation of methane could react with radicals from coal thereby causing alkylation of coal. Alkylated coal has been found to produce greater yield of benzene and pyridine soluble products than the untreated coal.[33]

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There is, yet, another possible factor to be considered in the inter-
actions of methane with coal in a solvent vehicle. The free radicals pro-
duced from the methane will either react with the solvent, the coal, or
even the methane itself. This would tend to increase the total liquid and
gaseous yield in the system. Thus, it may be expected that not only will
the coal be converted to liquid hydrocarbon products, but the makeup feed
material also would be converted to valuable higher hydrocarbon products.
The economic attractiveness of the entire process should, therefore,
improve.

No experimental data on the use of methane in direct liquefaction of
coal exist in the literature. In an effort to define the possible role of
methane in the conversion of coal to liquid products, experiments were
conducted with an Illinois No. 6 coal, designated as PSOC-1098 in Penn
State/DOE coal data base. An analysis of the coal employed in this inves-
tigation is given in Table 1.

Detailed description of the construction and operation of the tubing
bomb reactor is available.[34] The liquefaction conditions were as
follows: 2.5gm coal + 7ml tetraline as donor vehicle, 400-425°C, gas
pressure (at temprature) 1400 psi, 30 minutes reaction time and agitation
at 400 min⁻¹. At the end of the reaction, the contents were cooled by
quenching the reactor in cold water and the gases were vented to the atmo-
sphere. The remaining products were rinsed out of the reactor into a
soxhlet trimble with ethyl acetate (EtoAc). This was then followed by ex-
haustive extraction of the products with EtoAc in a soxhlet apparatus for
24 hours. After removal of EtoAc in a vacuum oven, the residue was weigh-
ed to determine the total conversion. From a knowledge of the coal miner-
al matter content of coal, liquefaction conversion on a dry, mineral
matter free basis can be calculated.

Table 1

Analysis of PSOC-1098, Illinois No. 6 hvAb Coal

Proximate Analysis:				Ultimate Analysis:		
		daf	dmmf (Parr)			
% Volatile matter:		35.15			mm:	19.32%
% Fixed carbon :		48.99		C	80.20	83.64
% Dry ash :		15.86		H	5.73	5.97
				N	1.45	1.51
				S	4.73	
				Cl	0.06	0.06
				O (diff)	7.84	8.03

The liquefaction experiments in methane atmosphere were conducted
with bottled methane gas at 400, 425, and 450°C. The coal liquefaction
conversions to ethyl acetate solubles (oils + asphaltenes) plus gases were
71.3, 73.4 and 75.4% (dmmf) at 400, 425 and 450°C, respectively. These
data are plotted as a function of temperature in Figure 1. In comparison,
the liquefaction of the same coal at 425°C yielded 74.8% (dmmf) of gases

and liquids in the presence of hydrogen which is only slightly higher than in methane (73.4%) and 68.2% (dmmf) in nitrogen, which is considerably lower than in methane. Thus, the indication is that methane could be a potentially useful hydrogenation agent in direct coal liquefaction. A simplified process block-diagram of the various processing steps are shown in Figure 2.

A comparative assessment of the performance of the coal-methane system with the coal-hydrogen system under nominal liquefaction conditions, in various solvents, will be an important contribution to the emerging coal liquefaction science and technology. This study could lead to the development of alternate, new and economically attractive coal liquefaction processes.

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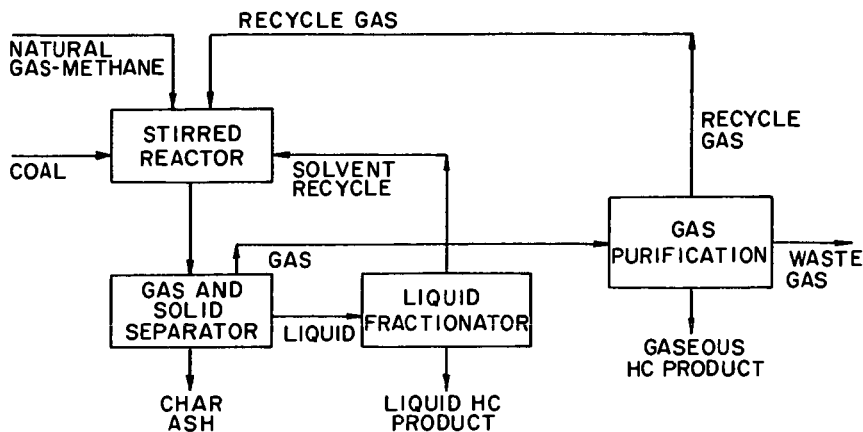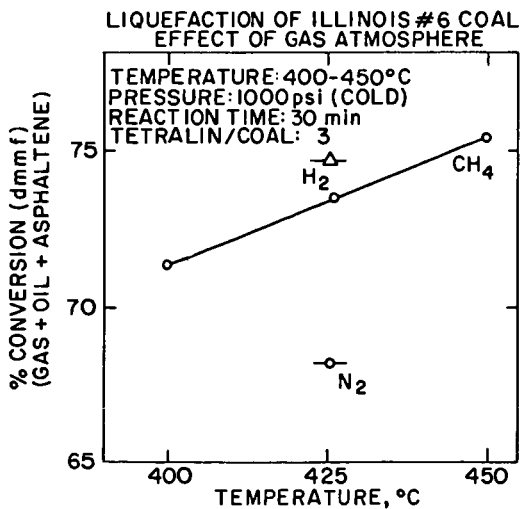
RECYCLE GAS

NATURAL
GAS-METHANE

STIRRED
REACTOR

COAL

SOLVENT
RECYCLE

RECYCLE
GAS

GAS
PURIFICATION

WASTE
GAS

GAS

GAS AND
SOLID
SEPARATOR

LIQUID

LIQUID
FRACTIONATOR

GASEOUS
HC PRODUCT

CHAR
ASH

LIQUID HC
PRODUCT

FIGURE 2.

LIQUEFACTION OF ILLINOIS #6 COAL
EFFECT OF GAS ATMOSPHERE

TEMPERATURE: 400-450°C
PRESSURE: 1000 psi (COLD)
REACTION TIME: 30 min
TETRALIN/COAL: 3

H₂

CH₄

N₂

75

70

65

% CONVERSION (dmmf)
(GAS + OIL + ASPHALTENE)

400   425   450
TEMPERATURE, °C

FIGURE 1.

Reaction of a Bituminous Coal with the Potassium-Crown Ether Reagent

Shuyen Huang, Karl Wood, and Ramani Narayan

Coal Research Center
Institute for Interdisciplinary Engineering Studies
Purdue University
A.A. Potter Engineering Center
West Lafayette, Indiana 47907

Introduction

It is generally accepted that a bituminous coal is best represented as a macromolecular, highly cross-linked, three-dimensional structure with aromatic clusters cross-linked by ether and alkane bridges and hydrogen bonds (1,2). Therefore, most coal conversion reactions involve reacting coal under severe conditions of temperature and pressure. As a result of the severe conditions, bond cleavage was nonselective and often accompanied by retrogressive (bond-forming) reactions. In this paper, we report on the reaction of a bituminous coal with a powerful yet selective site-specific reagent, namely, potassium-crown ether operating at *room temperature* and *atmospheric pressure*. The potassium-crown ether reagent can generate a stable solution of electrons at room temperature and atmospheric pressure (3,4). The small size of the electron and its high reactivity permits it to diffuse into the macromolecular coal network and transfer onto the aromatic substrates in the coal. This results in the formation of aromatic radical anions or dianions which undergo cleavage reactions at ether (5,6) and diaryl alkane linkages (7,8). Furthermore, crown ethers act as phase transfer catalysts in promoting the electron transfer to the solid coal. The reduction of the aromatic rings to dihydro or tetrahydro products occurs along with the cleavage reactions (9).

Experimental

A 250 ml round bottom flask was flame dried and flushed with nitrogen. Potassium metal (2.96 g, 75 mmole) was cleaned and cut under hexane and transferred into the round bottom flask in a nitrogen atmosphere glove box. The flask was again flame dried and flushed with nitrogen to remove traces of hexane. 100 ml THF solution of crown ether (4.0 g, 15 mmole) was added to the potassium metal via a double-ended needle. A dark blue solution was obtained which was cooled to $0^{o}C$ in an ice bath for 30 minutes. One gram of Illinois No. 6 coal (C=74.69%; H=5.44%; N=1.88%;O=18.06%; 100 mesh) was added to the K-CE/THF solution using a transferring tube which was originally attached to the round bottom flask. The reaction mixture was stirred for 48 hours under nitrogen at room temperature. It was then cooled to $0^{o}C$ and quenched with water. The THF was removed by rotaevaporation. The aqueous slurry of the coal was freeze-dried to remove the water. The work-up of the reacted coal is shown in Figure 1.

Results and Discussion

The Illinois No. 6 bituminous coal was reacted with the potassium-crown ether reagent at room temperature and atmospheric pressure. The reaction mixture was quenched with water and fractionated into THF extracts and alkali-solubles as shown in Figure 1. For each K-CE reaction, 15-20% of the coal was solubilized into THF and aqueous alkali fractions. After the third and fourth K-CE reactions, about 50% and 75% of the original coal was

solubilized, respectively. The formation of the alkali-soluble coal fragments indicated that ether linkages are being cleaved to form phenolic coal fragments.

Table 1. Total Solubility of Illinois No. 6 Coal
inr Each Fraction After Three and Four K-CE Reactions

| Notebook # | THF-1 (%) | ALK (%) | THF-2 (%) | Total Solubility | |
				Solubles	Residue
H2-52A (A-C) Three K-CE Reactions	9.9	26.9	14.7	51.5	51.2
H3-6 Four K-CE Reactions	13.7	51.6	12.8	78.0	22.8

The reason for successive K-CE reactions is due to certain limiting steps in the electron transfer process: (1) concentration of the solvated electrons in solution-more concentration of electrons, greater would be the transfer to the aromatic substrates in coal which in turn would mean greater cleavage and reduction reactions being initiated; (2) intrinsic repulsive barrier of the negatively charged aromatic substrates generally by the initial electron transfer; and (3) mass transport limitations. Obviously, one can increase the solubility of the coal into the various fractions by optimizing the potassium-crown ether to coal ratio, reaction time, temperature, and etc. However, successive potassium-crown ether reaction allows us to selectively snip at the macromolecular network at room temperature and atmospheric pressure conditions to prepare solubilized coal fragments with are amenable to detailed chemical, spectroscopic, chromatographic, and mass spectrometry analysis.

The elemental composition of each soluble fraction (THF-1, alkali, THF-2) and insoluble coal residue was determined by microanalysis. (Table 2). The hydrogen to carbon ratios are also included in Table 2. The results showed that after each K-CE reaction of coal there is an increase in the number of hydrogen atoms. The overall hydrogen uptakes are 7, 18, and 22 per 100 C-atoms for first, second, and third K-CE treatment, respectively. The hydrogen uptake is due to reactions such as Birch-Huckel-type reduction, cleavage of aliphatic bridges and ether linkages occurring during the K-CE reaction with coal.

Both THF extracts (THF-1 and THF-2) have higher H/C ratio as compared to the alkali soluble fraction and the insoluble residue during each K-CE reaction. A gradual increase in H/C ratio for each fraction after second and third consecutive K-CE treatment was also observed. This result corresponds well with the overall increase in hydrogen content and suggests further that reduction and cleavage of coal molecules upon additional K-CE treatment were occurring.

Figure 2 shows the infrared spectra of the various extracts obtained from the K-CE reaction with the coal. The IR spectrum of THF-1 extract was dominated by sharp aliphatic CH stretching bands just below 3000 cm^{-1} suggesting that this extract contains predominantly aliphatic material. This finding is in agreement with the high H/C ratio obtained for this extract. The spectrum of THF-2 extract also showed the dominating C-H stretching vibrations just below 3000 cm^{-1}; however, a broad OH stretching vibration in the

Table 2. Elemental Analysis of K-CE Treated Coal

| | Analysis (wt%) (daf) | | | | |
	C	H	N	O	H/C
Illinois No. 6 untreated coal	74.69	5.44	1.88	18.06	0.87
(1st K-CE Reaction)					
2-52A-THF-1	79.00	8.74	2.35	9.90	1.33
2-52A-Alk	71.76	5.90	1.55	20.77	0.99
2-52A-THF-2	74.02	7.04	0.81	18.14	1.14
2-52A-Res	73.23	5.95	1.28	19.50	0.90
(2nd K-CE Reaction)					
2-52A-THF-1	75.01	7.96	0.44	16.59	1.28
2-52A-Alk	68.34	5.97	0.90	24.80	1.05
2-52A-THF-2	67.93	7.22	0.56	24.20	1.28
2-52A-Res	74.12	6.27	0.71	19.70	1.02
(3rd K-CE Reaction)					
2-52A-THF-1	-	-	-	-	-
2-52A-Alk	71.00	6.67	0.99	21.34	1.13
2-52A-THF-2	70.67	7.51	0.77	21.05	1.28
2-52A-Res	73.00	6.54	1.02	1.94	1.08

Note: THF-1: THF extract of alkali residue
Alk: Aqueous alkali soluble fraction after THF-1 extraction
THF-2: THF extract of acidified residue after THF-1 and Alkali extraction

$3400\text{-}3200 \ cm^{-1}$ was also present. Thus, the THF-2 extract also contains aliphatic material which may be attached to a hydroxy aromatic ring system. Again, the increased H/C ratio nicely corroborates the presence of aliphatics. Both THF extracts showed carbonyl absorptions around $1710 \ cm^{-1}$. The alkali-soluble fraction showed a strong carbonyl stretching vibration at $1700 \ cm^{-1}$ coupled with a broad O-H stretching vibration extending down from $3500 \ cm^{-1}$. The infrared spectrum of the residue was similar to the untreated coal but showed weak carbonyl absorption bands.

The carbonyl absorption bands present in the IR spectra of all the extracts suggests that reduction of phenolic units to cyclohexanone (i.e., OH to C=0) units was a major reaction pathway in the reaction of coal with the K-CE reagent. The reduction of phenols and naphthols to the corresponding dihydro or tetrahydro aromatic carbonyl compounds by the K-CE reagent has been confirmed by us using model compounds. More work needs to be done to clarify the reaction mechanism; however, the increased hydrogen content of the alkali soluble and residue fractions on consecutive K-CE treatments of coal supports this reduction chemistry. The reasons for the carbonyl components to be fractionated into an alkali soluble fraction, an insoluble residue fraction, and in the THF extracts are: (1) carbonyl units that can undergo a keto-enol-tautomerism would be rendered alkali soluble; (2) the cyclohexanone type units which are hooked to coal phenolic units would also be alkali soluble; and (3) the carbonyl components in the THF extracts would be the relatively nonpolar components.

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Figure 3 shows the proton NMR spectrum of the THF-1 extract. The spectrum confirmed the presence of predominantly aliphatic material in this extract. Thus, the dominant sharp signal at 1.2 ppm is characteristic for methylene protons of long-chain polymethylenes. The group of signals in the 2-3 ppm region can be assigned to dihydro aromatic protons. Based on the mechanism of the K-CE reaction reduction of the aromatic ring to dihydro and even tetrahydro aromatics was expected and the NMR evidence nicely corroborates it. Thus, one of the major constituents of this extract is long-chain polymethylenes which may or may not be attached to a hydroaromatic ring system. The ^{13}C NMR spectrum (Figure 4) also strongly supported the presence of long-chain polymethyelene groups in the extract. The most intense signal is at 30.2 ppm which is generally assigned to the internal methylene carbons of straight-chain alkanes (an average carbon chain length of approximately 8). The presence of a broad spectral envelope in the 15-50 ppm region in addition to the sharp alkane lines is indicative of the extract's complexity arising out of the presence of only small amounts of these polymethylene-type compounds. The broad complex band of carbon signals in the 120-130 ppm region is due to the aromatic and polycyclic aromatic species of the extract.

Detailed characterization of the polymethylenes in the THF-1 extract was done using chemical ionization mass spectrometry and tandem mass spectrometry (MS/MS) (10,11). Tandem mass spectrometry is a well-established technique for the direct analysis of complex mixtures, because it can do unaided separation and identification of the constituents of the mixtures. By using different scan types, the structure of individual components can be identified and the presence of series of related compounds can be ascertained. In particular, daughter scans identify specific constituents of the mixture on the basis of molecular weight and fragmentation behavior.

Figure 5 shows the CI mass spectrum of the THF-1 extract. In it, one can identify 14 sets of three intense peaks; each set separated by 14 amu. Based on the molecular weight, the first set of three peaks at m/z 129, 131, and 133 can be assigned to the protonated molecular ions of naphthalene, dihydronaphthalene, and tetralin. It follows that the remainder sets of three intense peaks represented the homologous series of alkylnapthalenes, alkyldihydronaphthalenes, and alkyltetralins, with the polymethylene chain extending up to 14 carbons (Figure 6). In all probability, the dihydronaphthalene series and the tetralin series arise by *Birch Reduction* of the naphthalene compounds during the K-CE reaction. Therefore, only the homologous series of alkyl naphthalene compounds may be present in the coal. There are other molecular ions present but their intensities are well below that of the naphthalene-polymethylene series.

It was indeed surprising to obtain such a clean CI mass spectrum in which the polymethylene molecular ions predominate. Normally, mass spectra of coal mixtures is complex and messy and no clear-cut compound series can be identified. The reason we obtained such a clean spectrum is because the analysis was done on the THF-1 extract obtained from the second K-CE reaction. In the first K-CE reaction all the extractable material in coal and other compounds associated with coal will be removed during the THF extraction, alkali extraction and another THF extraction steps, leaving behind a *pristine* coal macromolecule. This strongly implies that the polymethylenes are not present as "trapped molecules" but as an integral part of the coal macromolecular matrix. The polymethylene chain could be present as crosslinks between aromatic clusters or as long dangling side chains on an aromatic ring.

Daughter spectra (Electron Impact) were taken for each and every member of the homologous series to confirm the structural identity of the polymethylene compounds.

Summary

The reaction of a bituminous coal with the K-CE reagent resulted in the selective sniping of the linkages in the coal macromolecular network at *room temperature* and *atmospheric pressure*. Soluble chunks of coal fragments were obtained without recourse to any thermal or pressure effects. In addition to ether cleavage reactions, a major reaction pathway in the coal/K-CE reaction is the reduction of phenolic groups to carbonyls. Analysis of the THF-1 extracts revealed the presence of a homologous series of alkyl naphthalenes and alkyl tetralins, with the methylene chain extending up to 14 carbon atoms, as the major components in the extract. These compounds are *real* and an integral part of the coal matrix and not present as *trapped molecules*. Any representation of *coal structure* or the development of *coal process models* would have to account for these pockets of *aliphatic rich zones*.

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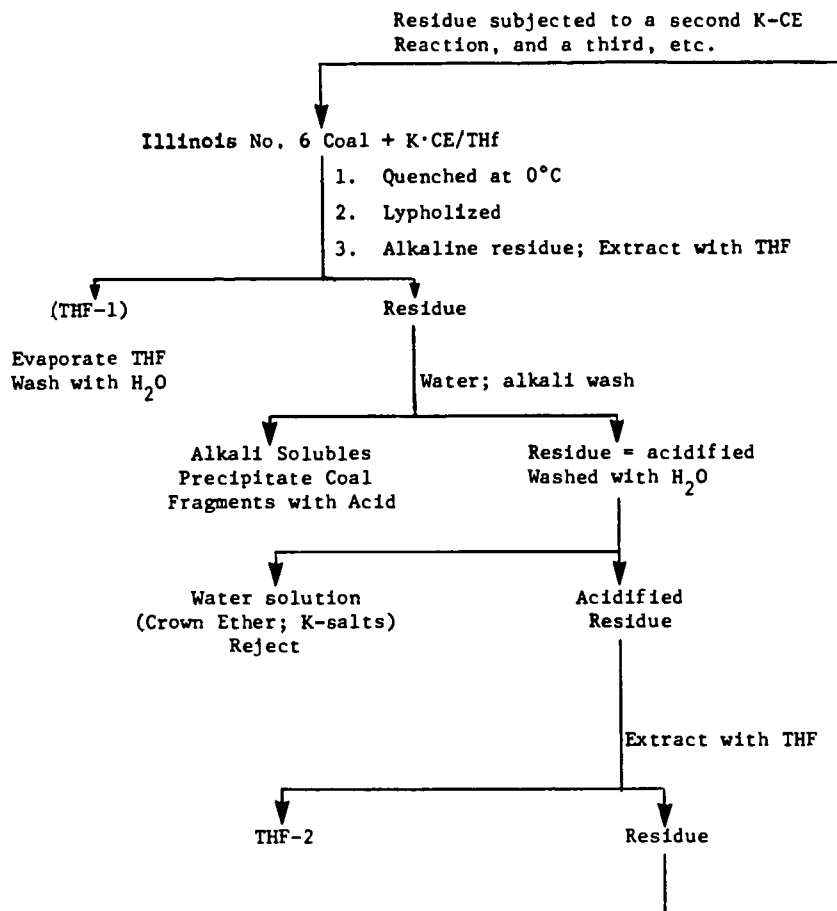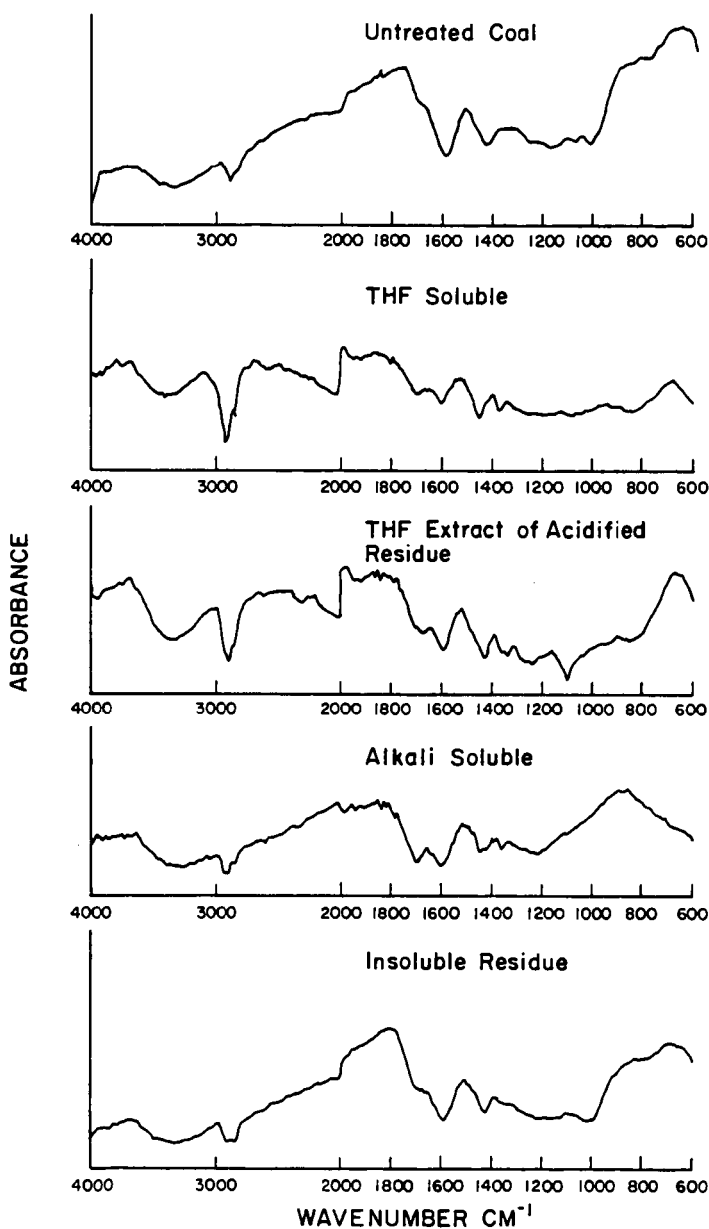
Residue subjected to a second K-CE
Reaction, and a third, etc.

Illinois No. 6 Coal + K·CE/THf

1. Quenched at 0°C

2. Lypholized

3. Alkaline residue; Extract with THF

(THF-1)   Residue

Evaporate THF
Wash with H_2O Water; alkali wash

Alkali Solubles   Residue = acidified
Precipitate Coal   Washed with H_2O
Fragments with Acid

Water solution   Acidified
(Crown Ether; K-salts)   Residue
Reject

                                    Extract with THF

THF-2   Residue

Figure 1. Work-Up of the Coal/K-CE Reaction.

Figure 2. Infrared spectra of different fractions of K-CE treated Illinois No. 6 Bituminous Coal.

THF
Soluble
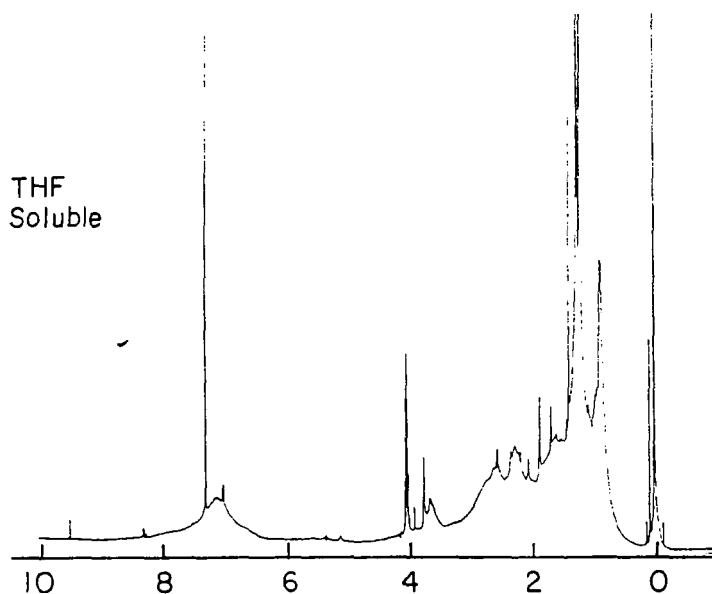
Figure 3. ^{1}H NMR of THF-1 extract.

THF Soluble
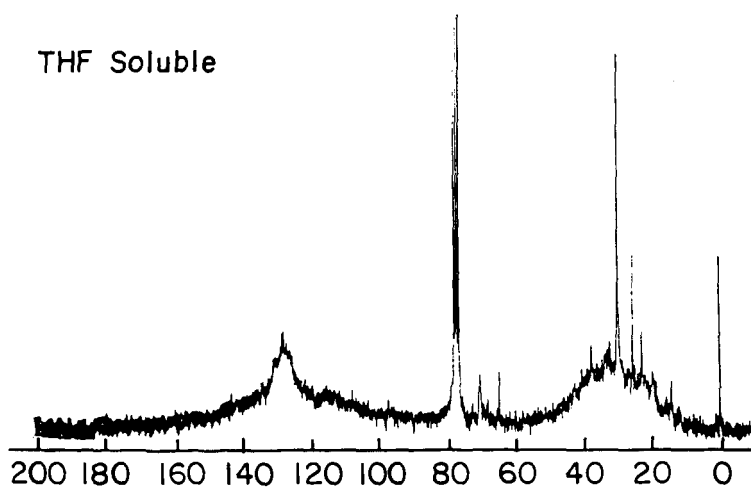
Figure 4. ^{13}C NMR of THF-1 extract.
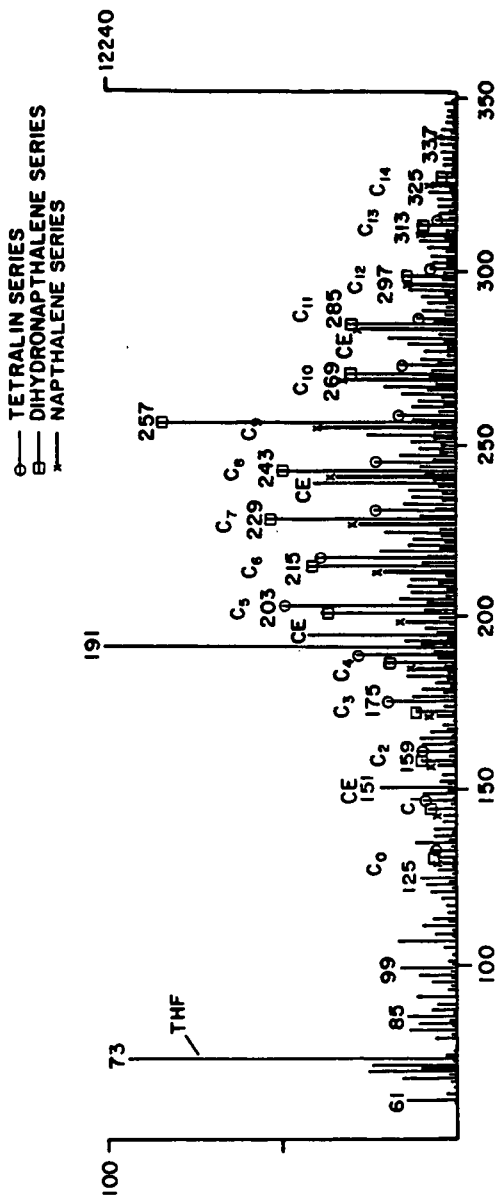
Figure 5. Chemical ionization mass spectrum.

Dihydronapthalene Series

Tetralin Series

Napthalene Series

n= 0,1,2,3,4,.......14

n= 0,1,2,3,4,5......14

n= 0,1,2,3,4.......16
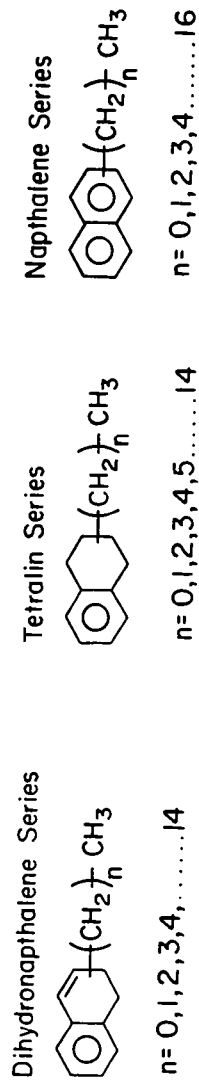
Figure 6. Polymethylene structures in coal.

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MILD OXIDATIVE SOLUBILIZATION OF COAL MACERALS

Randall E. Winans, Ryoichi Hayatsu, Robert L. McBeth,
Robert G. Scott and Robert E. Botto

Chemistry Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439

The objective of this study is to solubilize coal macerals and an Argonne Premium Coal Sample using oxidation and to characterize these soluble products. A major problem in coal characterization and in coal utilization is the intractability of the coal macromolecular network. High temperature treatments yield smaller, volatile and soluble molecules, which can be greatly altered from their original structures, along with a significant amount of a non-volatile char. Mild oxidation should provide a soluble mixture of compounds in higher yields and with structural characteristics more like the original coal. The approach described in this paper attempts to oxidatively cleave only activated benzylic sites in the coal macromolecules in a two step process. In the first step benzylic sites which are partially active due to oxygen functionality either on the aromatic ring or on the benzyl carbon are further activated by the formation of pyridinium salts at that carbon from the reaction with pyridine and iodine. In the second step this carbon is oxidized by alkaline silver oxide resulting in formation of carboxylic acid groups. This process has been described in an initial communication for whole coals (1) and the results of the first reaction on the macerals, used in this study, has been published (2). This report will focus on the yields of the oxidation step and the characterization of the products.

A few oxidative degradation studies on separated coal macerals have been published (3-5). In these studies there was extensive oxidation and only small molecules were identified. In this study, both smaller and higher molecular weight fractions which were separated on the basis of solubility have been characterized using gel permeation chromatography (GPC), GCMS, Pyrolysis MS (PyMS) the precise mass measurement mode, Fast Atom Bombardment (FAB) MS, and NMR. FAB MS has proven to be useful in the characterization of polar biological compounds. This is the first application of this technique to coal oxidation products. Since FAB is a relatively mild ionization technique, it should help to characterize products with molecular weights greater than 500. Compounds in this range are not volatile enough for GCMS and are broken down into smaller fragments by PyMS. However, the chance of rearrangements in PyMS are reduced when pyrolysing the oxidation products in comparison to the whole coals or maceral concentrates. It is interesting to note the remarkable lack of large polycyclic aromatics in the soluble products. The significance of this result will be discussed.

EXPERIMENTAL

Samples

A description of the macerals and whole coal is given in Table 1. Details of the maceral separation have been reported (2). The Upper Elkhorn and the Brazil Block samples have been separated from coals obtained from Pennsylvania State University labelled PSOC 1103 and PSOC 828, respectively. The subbituminous coal is the Argonne Premium Coal Sample (APCS) number 2, which has been recently mined and has been stored under nitrogen in sealed glass ampules. The preparation of the oxymethylene linked polymer(I) has been described (6).

(I)
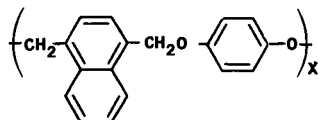
Oxidations

The pyridinium salts of the samples were prepared by refluxing 1 g of the coal, maceral or polymer in 60 ml of pyridine with 4 g of iodine for 70 hrs (2). The reaction mixture was poured into 10% aqueous $NaHSO_3$ and the solution filtered. The derivatized coal was washed free of pyridine, dried and analyzed. In a typical oxidation fresh Ag_2O, prepared from 8.5 g of $AgNO_3$ and sodium hydroxide, was refluxed with 1.0 g of the substate in 50 ml of 10% aqueous NaOH for 20 hrs. The silver and unoxidized samples were removed by filtration and the filtrate acidified with aqueous HCl. Products which were alkaline soluble but insoluble in the slightly acidic solution were termed humic acids. The solubles were extracted with Et_2O-MeOH. Yields were determined by analysing the products for carbon. The products were methylated with diazomethane for further analysis.

Characterization

Approximate molecular size distributions were determined by gel permeation chromatography using a set of three ultra-Styragel columns with 100, 500, and 1000 Å nominal pore diameters. The samples were eluted with THF and detected by UV at 254 nm. The columns were calibrated using a set of esters of known molecular weight.

GCMS and PYMS data were obtained on a Kratos MS-25 mass spectrometer. A 60 m x 0.25 mm DB-1701 fused silica column was used in GCMS analysis. The details of the PyMS experiment have been reported (2). The samples were all heated at 50°/min on a platinum screen and the instrument was operated in the precise mass measurement mode. The FABMS data were obtained on a VG 70-250 at the University of Chicago, Chemistry Department. Argon gas was used with glycerol as the probe matrix. NMR data were taken on a Bruker AM-300 using $CDCl'_3$ as a solvent.

RESULTS AND DISCUSSION

The yields for the oxidation step are very sample dependent as is shown in Table 1. The yields are calculated based on the carbon content of the starting material and of the products with the values given being an average of at least two experiments. The oxidation of the Illinois No. 2 vitrinite yielded 84% of the original carbon in the soluble products. This result can be contrasted with the fusinite where only 47% of the carbon has been recovered of which 40% was the Et_2O/MeOH soluble fraction. If one assumes that fusinite is "fossil charcoal", then this result is expected. The number of pyridinium salts formed (1.5/100 carbons) is small and suggests that much of the oxygen occurs as heterocyclics. In addition, there were probably less benzylic carbons in this fusinite compared to the vitrinite. The lower yield for the sporinite, 62%, compared to the vitrinite may reflect

the greater aliphatic content of the sporinite which would be resistant to oxidation. The APCS #2 has a similar composition to the Illinois No. 2 vitrinite and yields essentially the same amount of solvent solubles but less humic acid material. Oxidation of the polymer gives only 1,4-naphthalenedicarboxylic acid. No evidence the naphthalene ring oxidation has been found. It is interesting to note that one naphthalene-dicarboxyic acid is formed for every pyridinium salt.

The Et_2O/MeOH soluble fraction does have a significant amount of higher molecular weight materials as is seen in the GPC data from the methyl esters presented in Figure 1. The molecular size scale is only approximate and this approach works best for comparisons. Figure 1a compares Illinois No. 2 vitrinite with fusinite. The fusinite gives a narrower distribution shifted to a larger molecular size compared to the vitrinite. A comparison of the solvent solubles and humic acid from Upper Elkhorn vitrinite is shown in Figure 1b. The humic fraction higher MW peak is significantly higher than the corresponding peak for solvent soluble. Since this is a fairly mild degradation the molecular size distribution is typically at a much higher MW compared to pyrolysis products of the sample samples. Finally, it is interesting to note the difference in Figure 1c of the output from a UV and a fluorescence detector which are in-line. The chromograms have been normalized, but the poor signal-to-noise from the fluorescence detector is a good indication of the lack of fluorescing compounds such as polycyclic aromatics in the product.

Proton NMR data lends support to the observation of the lack of polycyclic aromatics. Since even the solvent soluble fractions contained compounds which are too large and non-volatile for GCMS, the proton NMR spectra have been taken. The methyl ester region is the most informative and is shown for the Illinois No. 2 samples in Figure 2. From the spectra of a number of known methyl esters, three regions can be assigned: 3.6-3.8 aliphatic, 3.8-4.0 single ring aromatics and heteroaromatics, and 4.0-4.2 polycyclic aromatics and heteroaromatics. Single-ring aromatics and aliphatics are the most abundant species in these samples.

Compounds that can be separated by GCMS are mostly benzene, and hydroxybenzene carboxylic acids. The total ion chromatogram for APCS #2 is shown in Figure 3. Although this is a fairly mild oxidant, tetra-, penta- and hexa carboxylic acids are still formed. Also note even the hydroxybenzene tetra- and penta-carboxylic acids are formed. More model compounds are being examined to better understand this result. In addition to benzene and hydroxybenzene carboxylic acids, furan carboxylic acids are found in significant abundance.

Fragments found by PyMS with APCS #2 and the vitrinites are dominated by aliphatics and single ring aromatics and hydroxylated aromatics. PyMS of the humic products results in volatilization at lower temperatures as compared with the coal or maceral, as is shown in Figure 4. Comparing the pyrolysis products between the two samples, the most striking difference is the reduction in aliphatics in the humic acid fraction. Figure 5 shows the distribution of hydrocarbons found as a function of Z-number (hydrogen deficiency, 0-alkane, 1-alkene, 4-benzene, etc.). However, in each case the contribution of fragments with more than 1 aromatic ring was small, 5.6% for the coal and 4.6% for the oxidation product. A milder ionization approach has been taken with some of these samples. A FAB MS spectrum for the solvent solubles from the Upper Elkhorn vitrinite is shown in Figure 6. Again, peaks which can be identified as single ring compounds dominate. However, unlike electron impact peaks are seen at M/Z > 400. The conditions for this experiment need to be optimized and a matrix more suitable than glycerol used. Also, some of these samples will be analysed using field ionization MS.

All of these results strongly suggest that for our vitrinite samples and the subbituminous coal sample the single ring aromatics dominate. Unlike many other experiments most of the carbon is characterized using this approach. More model compounds and polymers are being studied to verify the selectivity of this derivatization/oxidation procedure.

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TABLE 1. Coal and Maceral Samples.

Sample ( )[†]	Source	Rank	Empirical Formula	$Py^+/100°C$	Ag$_2$O Oxidation Yields*	
					Organic Soluble %	Humic Acid %
APCS #2	Rawhide Seam	Subbituminous	$C_{100}H_{87}N_{1.4}S_{0.4}O_{19.6}$	4.1	~40	26
Vitrinite (95+)	Illinois #2	HvC Bituminous	$C_{100}H_{87}N_{1.5}S_{0.8}O_{18.3}$	3.8	44	40
Fusinite (95+)	Illinois #2	HvC Bituminous	$C_{100}H_{64}N_{0.8}S_{1.1}O_{11.3}$	1.5	40	7
Vitrinite (93)	Upper Elkhorn	HvA Bituminous	$C_{100}H_{83}N_{1.9}S_{0.5}O_{10.5}$	4.6	--	--
Sporinite (91)	Brazil Block	HvA Bituminous	$C_{100}H_{115}N_{1.2}S_{0.8}O_{10.7}$	3.8	46	16
Polymer-I			$C_{18}H_{14}O_2$	2.4	44[+]	

[†]Maceral petrographic composition.
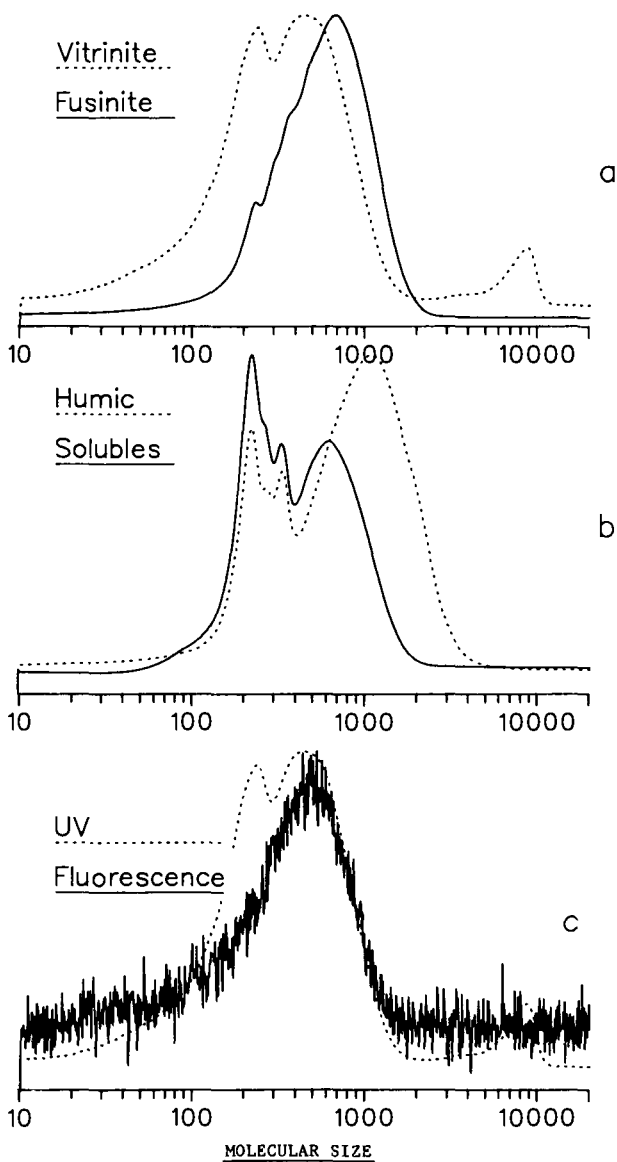*Based on carbon composition.
[+]Mole percent.

Figure 1. Gel permeation chromatograms of methyl esters: a) Illinois No. 2, solvent soluble fraction; b) Upper Elkhorn No. 3 vitrinite, and c) Illinois No. 2 vitrinite solvent soluble fraction.
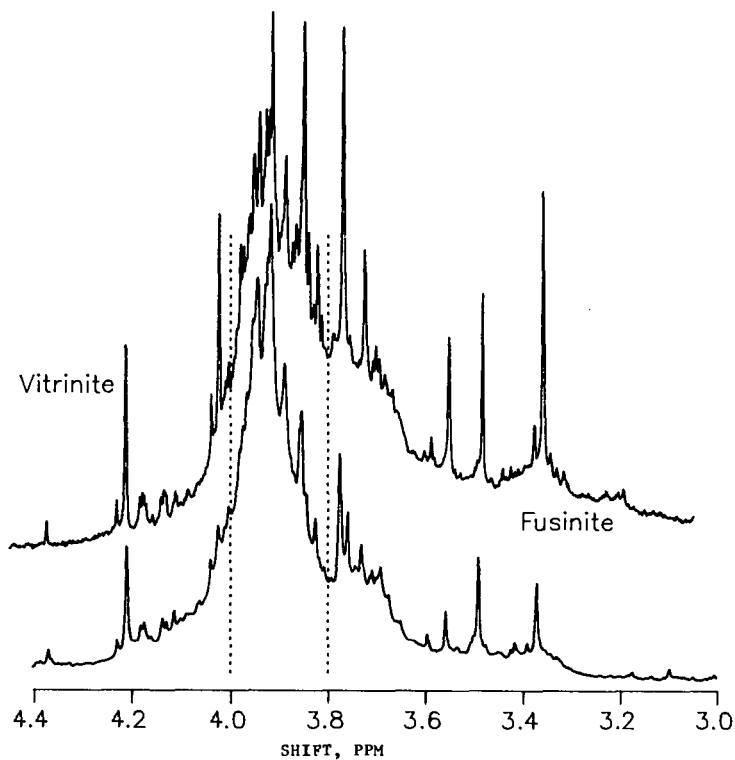
Figure 2. ¹H NMR spectra of Illinois No. 2 solvent soluble fraction, esters.
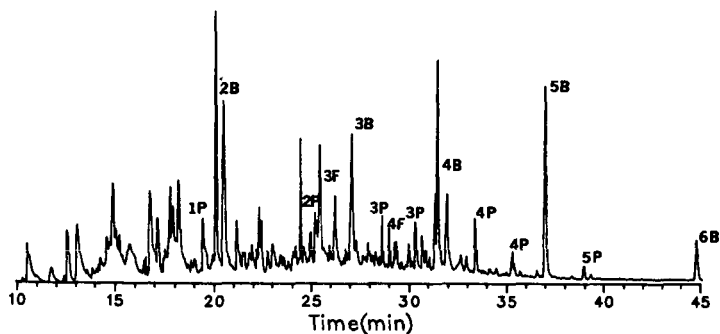

Figure 3. Total ion chromatogram of APCS #2 solvent soluble fraction, methyl esters. Major peaks: 2B-6B number of carboxylates on benzene, 2P-5P number on phenol and 2F-4F number of carboxylates on furans.

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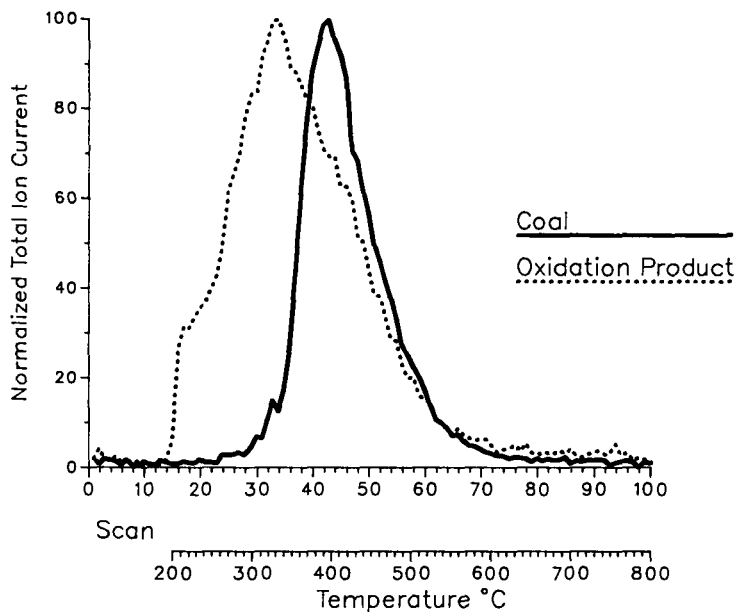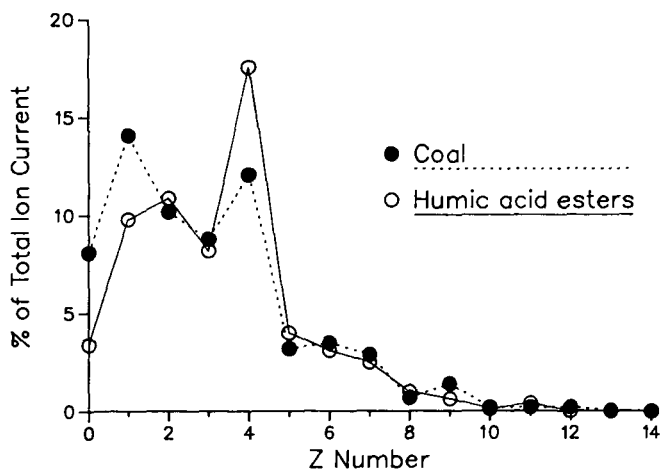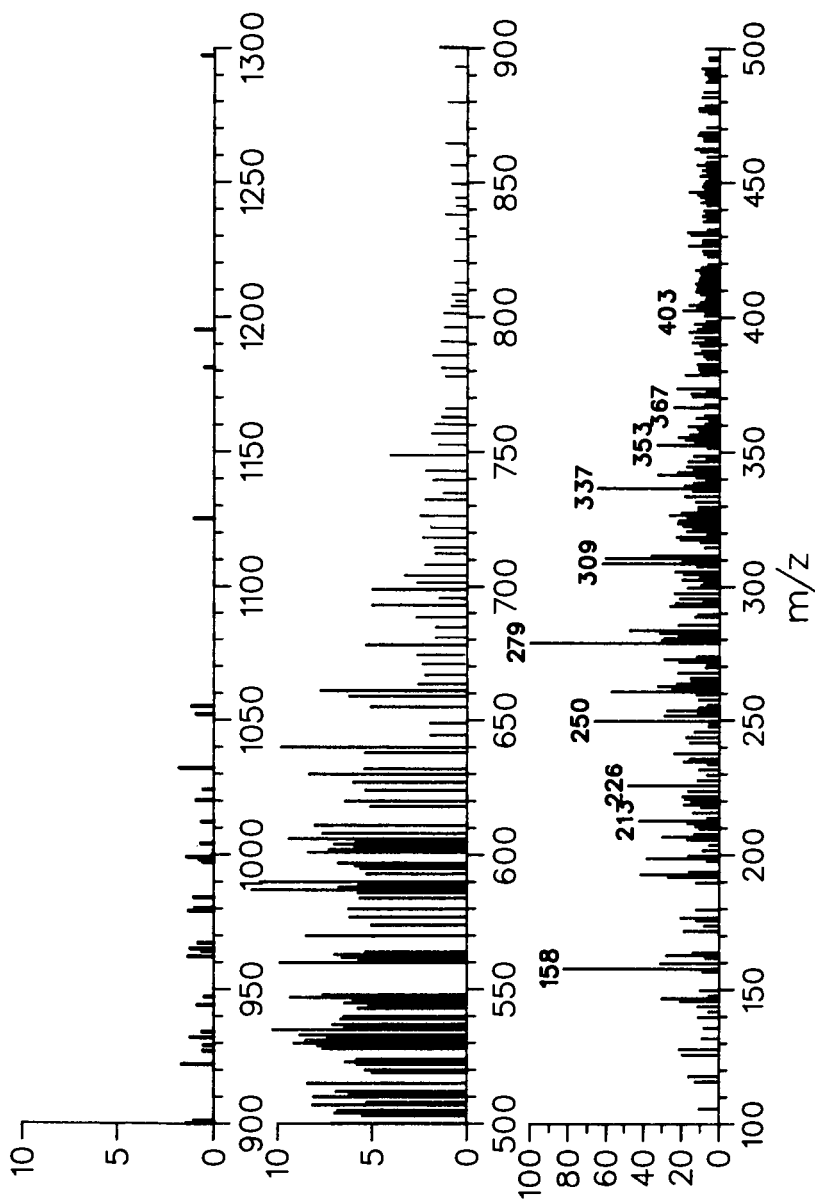**Figure 4.** Total ion pyrograms for APCS #2.

Figure 5. Distribution of hydrocarbons with Z-number for average of the data shown in Figure 4.

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Figure 6. FAB mass spectra of Upper Elkhorn No. 3 vitrinite solvent soluble fraction, methyl esters.

Coal Oxidation and Thermal Chemistry

J. S. Gethner

Corporate Research - Science Laboratories
Exxon Research and Engineering Company
Annandale, NJ 08801

I. Introduction

The physical and chemical properties and processing characteristics of most coals are extremely sensitive to storage conditions.(1-3) Both drying and the air induced oxidation are known to produce substantial changes to coal. Consequently, they have been the subject of study throughout the history of coal research. In this paper we discuss some of the recently obtained data indicating that these processes involve a few simple chemical transformations which are closely coupled by virtue of their kinetic behavior. In-situ FT-ir analysis used to examine the overall chemical changes is examined herein. Light and neutron scattering were used to examine the concomitant structural changes thereby providing some information on the location of some of the reactive functionality within the coal matrix. These studies will appear elsewhere.(4-7)

Drying is believed to result principally in the loss of adsorbed water, though some studies suggest that chemical alterations occur. That drying produces some alteration is evidenced by the routine use of drying prior to almost all coal studies or processing. The de-facto standardization leads to a coal having reproducible characteristics. Despite considerable study, similar standardized procedures to mitigate the effects of oxidations are not currently available.

Since oxidation of coal is generally believed to influence many coal properties, the resulting literature is extensive. The principal cause of changes associated with the "weathering" of coal is attributed to oxidation. From a utilization standpoint, air oxidation alters properties of the coal which, depending upon the particular end-usage of the coal, may either be detrimental or advantageous. For example, the heat content of coal decreases upon oxidation resulting in increased amounts of coal being needed in any particular application. However, oxidation increases the heteroatom content of the coal resulting in a greater number of sites available for chemical reaction and catalyst binding. Changes to the swelling and fluidity properties of coals are correlated to oxidation. This implies that oxidation alters the fundamental geometrical structure of the coal in addition to the chemical composition and will likely have a secondary effect on all coal chemical reactions through induced alteration of mass and thermal transport through the "semi-solid" coal.

In order to understand these complex reactivity/structure relationships, we have examined both the chemical and structural changes which occur when a sub-bituminous (Rawhide - SBB) and a bituminous (Illinois No. 6 - HvC) coal are reacted at low-temperature (<150°C). In brief we find that drying produces chemical alterations which compete with some of the chemical reactions which occur during the oxidation. Oxidation consists of at least two separate sets of reactions which are distinguishable by their time and/or temperature dependencies. Correlations between the reactivity studies and structural studies carried out with scattering methods suggests the species which react both thermally and oxidatively reside on void surfaces and are readily accessible to the environment.(7-9)

In this paper we review some of our evidence supporting the presence of multiple competing thermal and oxidation reactions. The correlated structural studies are available elsewhere.(8,9)

II. Experimental

Experimental procedures employed are described elsewhere.(4,5,7) As previously describes, samples employed for FT-ir studies are thin sections having a nominal thickness of 0.4 micro-meters and an area of approximately 1 mm^2. Analytical data representative of the samples are contained in Table 1. A two-dimensional matrix of these sections is prepared using serially cut sections to obtain the desired total sample area on an appropriate substrate.

III. Results and Discussion

We have found that several reactions take place at low-temperature when dry coal is either heated or exposed to oxygen. In order to examine the oxidation chemistry, it is first necessary to remove the effects of drying. We therefore discuss the thermally induced changes prior to dealing with the oxidation.

Drying Results in decarboxylation/decarbonylation

The effect of drying on thin-section samples of Rawhide (SBB) and Illinois No. 6 (Hv-C) coals were examined in a series of experiments. The coal thin-sections were dried at room temperature by subjecting them to a moderate vacuum ($>10^{-5}$ torr) for at least 12 hours. Observation of the hydroxyl stretching region indicates that the physisorbed water is removed within the first hour. We believe that such vacuum drying is able to remove most of the water for two reasons: 1) O'Rourke and Mraw found that room-temperature "drying" of coal using a highly desiccative environment was capable or removing greater that 98% of the adsorbed water from powdered samples of similar coals[10] and 2) we find that subsequent drying by heating under vacuum at 100°C does not further reduce the hydroxyl stretching region intensity.

An example of the effect of heating such a dried Illinois No 6 coal sample for ca 6 hours under vacuum is shown in Fig. 1. Only the region of the ir spectrum indicating carbonyl content (C=O stretch and -C-O-H modes) is shown. The difference spectrum clearly indicates loss of carbonyl intensity at ca 1707 cm^{-1}. This region of the spectrum does not uniquely identify the specific carbonyl species lost. We assign the loss to hydrogen bonded or dimerized aliphatic carboxylic acids based upon several lines of reasoning. These will be discussed subsequently.

The observed frequency loss at ca 1707 cm^{-1} is generally assigned (9) to the C=O stretch in dimers of aliphatic carboxylic acids in which the aliphatic chain is contains more than 3 carbons.(11) It can also be assigned to a variety of ketone and aldehyde species. It is unusual for aromatic carbonyls to absorb at such a high frequency. This fact together with surface functionality information obtained from neutron small-angle scattering (8) makes an assignment to aromatic carbonyl functionality less plausible. Despite the possiblility that the absorption is due to non-carboxylic acid carbonyl species, the weight of the evidence summarized below is in favor of the carboxylic acid assignment. A more complete discussion of alternate assignments is available elsewhere.(6)

A spectral loss is observed at 1285 cm^{-1} which is observed to follow the same kinetics as the 1707 cm^{-1} loss feature. Therefore these two absorptions probably result from different vibrational modes of the same species. When present in addition to a carbonyl stretch, the 1285 cm^{-1} mode is diagnostic for carboxylic acid dimers. We have attempted to determine whether the reactive functionality was located on the void surface or inside the organic matrix by performing solvent permeation studies and examining the induced structural changes and permeability restrictions using neutron and light scattering techniques. Neutron scattering measurements suggest that aliphatic carboxylic acid species are present on the void (pore) surface.(8) In view of our spectroscopic assignments above, we believe the thermally reactive carboxylic acid species to be located at the pore surface.

Restricted mobility of both of reactant and product molecules within the coal matrix is expected. Indeed, higher temperature pyrolysis of coal shows that different chemical transformations occur when carried out under vacuum as compared to a closed atmosphere.(12) This is understandable when the overall reaction is the result of secondary reactions of some initially formed reactive intermediate. We investigated this by carrying out the same thermal reaction in a closed cell under a static helium atmosphere. The overall thermal reaction was unchanged. Only minor changes in some of the relative intensities of the absorption losses were seen. This indicates that mass transport limited secondary reactions are not important under these conditions. Therefore the thermal reaction is either 1) bimolecular between two topologically adjacent portions of the matrix or 2) sequential with the first step being the formation of a reactive species by a unimolecular decomposition followed by reaction with a nearby portion of the matrix surface. The available data does not uniquely determine either possibility.

Available functional group analysis of the Illinois No. 6 coal used for the experiments discussed above indicates that only a relatively small amount of carboxylic acid functionality (0.5 COOH per 100 carbon atoms) is present. We are not currently able to quantify the number of carbonyl groups which we observe since an extinction coefficient for these vibrations is not available for species present in a similar environment. Therefore we were particularly interested in observing the thermal behavior of a lower rank coal containing a larger carboxylic acid content. Rawhide coal containing ca 3.2 COOH per 100 carbon atoms was used.

In contrast to that observed for the Illinois coal, a significant loss of intensity which could be assigned to a loss of C=O species was not seen. There are several possible explanations: 1) carboxylic acid species are unreactive; 2) the predominant carboxylic species are not dimers and the carboxylic acid species which do react form some other carbonyl containing species (e.g., ketones or aldehydes); or 3) the absorptivity of the affected carbonyls is small. We discount 3) since observed C=O stretching intensities are strong in liquid, polymer and solid systems. In order to distinguish between 1) and 2), we employed pyridine as a spectroscopic titrant for acid functionality.

Several of the ring-based carbon vibrations of pyridine are sensitive to the existence and strength of any hydrogen-bonds formed with the unpaired electrons on the nitrogen. Such spectroscopic information has been used for investigations of acidic functionality on surfaces.(13) We show the dependence of some of the pyridine-based vibrations on thermal treatment in Fig. 2. Absorptions at 1485 and 1465 cm^{-1} characterize pyridine which is hydrogen bonded to two types of sites which differ in the strength of the hydrogen bond formed. Only one type of hydrogen bonded pyridine is seen prior to thermal treatment (1485 cm^{-1}). After thermal treatment two pyridine binding sites are seen. The original 1485 cm^{-1} absorption is narrower following thermal treatment. Therefore thermal treatment has converted part of the acid functionality associated with the 1485 cm^{-1} vibration to an acid center characterized by the 1465 cm^{-1} absorption and having a greater hydrogen bond strength than the original species. It is generally believed that the only significant acidic functionality present is phenolic and carboxylic.(1) Concomitant spectroscopic changes indicating phenolic reaction (e.g., 1600 cm^{-1} loss) is not observed. In addition the frequency loss (1485 cm^{-1}) indicates that the original species bound to pyridine have similar hydrogen bond strength. Therefore we assign the acid group loss to carboxylic species. Since corresponding loss in the C=O stretching region does not occur, we conclude that a reaction of the type

$$-(C=O)-OH + MATRIX \text{ or } ENTRAINED \text{ } SPECIES \longrightarrow -(C=O)- \qquad (I)$$

occurs. If the species which reacts with the carboxylic acid is a part of the "solid" matrix, a new covalent "cross-link" will be formed at the expense of one hydrogen-bonded "cross-link".

Oxidation of thermally treated coal at 100°C produces new oxygen functionality

The effect of O_2 oxidation of Illinois No. 6 coal at 100°C was examined. An example of the spectroscopic changes resulting from O_2 oxidation at 100°C is shown in Fig. 3 for a sample which had been thermally treated at 100°C to remove the reactive carboxylic acid species. The dependence of the oxidation changes on prior treatment (thermal, closed cell or ambient oxidation) was examined. The principal changes could be attributed to the same oxidation reactions indicating that the 100°C oxidation is reasonably independent of sample history.

The principal changes observed are absorption increases which occur in regions attributable to oxygen functionality on carbonaceous substances. Intensity increases in the carbonyl stretching region (1650 to 1750 cm^{-1}) indicates aldehyde, ketone or carboxylic acid formation. The observation that most of the intensity increase is broadly centered at 1670 cm^{-1} suggests that oxygen addition to aromatic or unsaturated carbon residues has taken place. Intensity increases occur in the "ether" region (1000 to 1150 cm^{-1} which, though not diagnostic for ether formation, are suggestive.

The reaction of coal with O_2 to form thermally unstable hydroperoxide intermediates has been frequently proposed as the principal air and/or O_2 oxidation reaction. Definitive spectroscopic evidence showing hydroperoxides has not been reported. Compelling non-spectroscopic evidence is reported by deVries, et al.(14) Our spectroscopic changes are consistent with the formation of all of the expected decomposition products of transient hydroperoxides with the exception of alcohols. Hydroperoxide decomposition proceeds by two parallel pathways: one leads to carbonyl formation while the other leads to alcohol formation. deVries found, and our data supports, the conclusion that the alcoholic pathway is not important in coal oxidation.

We do not believe that significant numbers of carboxylic acids are formed either. An increase in intensity in the OH stretching region associated hydrogen-bonding is not seen. Nor does acid group titration using pyridine indicate a change in the number of acidic groups as a result of oxidation. The principal reaction can be summarized as

$$(COAL)-C=C- + O_2 --> (COAL)-(C=0)-C- \qquad (II)$$
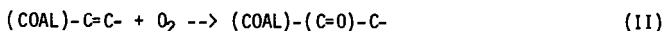
where we have indicated the reaction having occurred with unsaturated carbon as noted above.

A new oxidation reaction is found at room-temperature

The effect of lengthy O_2 on Illinois No. 6 coal was examined spectroscopically. While some changes were seen, they were of low intensity and difficult to resolve. Since the 100°C oxidation and the thermal decarboxylation are obviously independent reactions, we expected the room-temperature oxidation to have no effect on any thermal chemistry. This did not prove to be correct. Lengthy room-temperature oxidation eliminated all evidence of the thermal decarboxylation reactions. The room-temperature oxidation reactions, though not resulting in any striking absorptivity changes, have a dramatic reactivity effect.

We propose the existence of a hitherto unrecognized reaction which is competitive with the thermal decarboxylation reaction. The reaction is summarized as:

$$(Coal)-C=0 + O_2 ---> (Coal) + H_2O + CO_2 + CO \qquad (III)$$
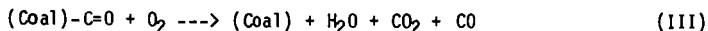
We have examined the kinetic behavior of this new oxidation reaction and find that the reaction is rapid by 50 to 60°C. On the other hand, the thermal decarboxylation

reaction is negligible below 60 to 70°C. Therefore there is a temperature "window" from approximately 50 to 80°C in which the reactions will compete and the overall spectroscopic and chemical changes are extremely sensitive to temperature and atmosphere. In addition we predict that any experiment employing a temperature-jump encompassing this temperature "window" will be heating rate dependent. Such a temperature-jump is routinely employed in coal drying procedures. A survey of the literature examining the low-temperature oxidation of coal reveals many statements that the coal used must be carefully predried under precisely defined conditions (see, for example, deVries, et al.(14) and the discussion and references in 7). We take this to be a consequence of the need to control these competing reactions. The sensitivity to the pre-oxidation conditions suggests that the reactivity differences arising from the thermal and room-temperature oxidation are significant even though the i.r. spectroscopic changes are relatively weak and non-specific.

Oxidation Mechanism

Based upon the above evidence with additional confirmation from studies not included herein, we propose the following "mechanism" for the low-temperature oxidation of coal. The oxidation at any moderate temperature is comprised of a combination of the reactions observed in the single-step procedures which we have discussed and summarized as I-III. Thermal decomposition results in loss of carboxylic acid functionality (I). These can be partially replenished during oxidation by the formation of a variety of new carbonyl species (II) resulting from the decomposition of transient hydroperoxide intermediates. The variety of carbonyl species formed is larger than lost due to the thermal decomposition. If the oxidation is allowed to proceed for a long time, the net change in carboxyl absorbance can approach zero. Consequently the net result of the thermal oxidation is to convert carboxylic acid functionality into a more extensive variety of oxygenated species. The oxygen-to-carbon ratio will be less sensitive to these changes than might be expected on first consideration since carbon may be lost through the production of CO and CO_2 and the change of carbonyl functionality will depend upon both the length of time allowed for reaction and the heating rate. A second oxidation reaction (III) occurs at a significant rate slightly above room temperature. Over some temperature ranges, this reaction occurs simultaneously with the thermal decomposition reaction (I) and is either competitive or involves a common intermediate species. Since the absorbance changes associated with II are relatively weak, reaction I will dominate the i.r. difference spectra when it is present.

Sensitivity to water content

We have observed that the relative contribution of the three indicated reactions is sensitive to water. This has not been systematically explored in our experiments. Similar dependencies have been reported.(14,15) deVries, et al.(14) point out that water will influence the hydroperoxide decomposition reactions. Marinov finds evidence for multiple reactions in the low-temperature chemistry of coal.(15) Marinov further finds that water is both a product and a reactant in the low-temperature chemistry of coal. Comparion of the conditions employed by Marinov and ourselves indicates that the two sets of observed reactions may be the same. Therefore water is likely involved in two or more of the reactions which we observe and will lead to extremely complex time-temperature-water content dependencies.

The conditions which we have employed and those of the other cited studies were carried out in the temperature range and using coals which are subject to "spontaneous" ignition. These complexities associated with water content will be one of several factors which will contribute to the initiation of such an uncontrolled oxidation. We believe that our results are suggestive of several new approaches which might be beneficial in preventing "spontaneous" ignition and, more generally, improving the stability of dry coal. Hydroperoxide oxidation is not important until relatively high temperatures and is endothermic in model compounds. Our identification of two additional reactions which occur at much more modest

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temperatures and are competitively coupled provides specific reaction-types which might be amenable to control. It is likely that interrupting either reaction will to improved coal stability and may even be effective in reducing or eliminating a key reaction leading to spontaneous ignition.

V. Conclusions

Analysis of FT-ir difference spectra obtained when coal is subject to different oxidation and thermal conditions indicates that thermal oxidation consists of at least three reactions all of which occur in a low-temperature (25 - 100°C) oxidation region. Reaction types (I-III) account for the observed data. Two of the reactions involve oxygen directly; the third is a thermal decarboxylation or decarbonylation reaction which proceeds in the absence of oxygen. Oxidation at 100°C results in the formation of a variety of oxygenated species. The principal products are believed to be carbonyl species which result from the decomposition of thermally unstable hydroperoxides formed by oxygen addition to some species in the coal. In contrast, oxidation at 25°C results in a net loss of absorbance which we interpret as a loss of carbonyl species. The thermal process results in significant i.r. absorption loss at frequencies which are characteristic of carboxylic acid species. Since carbonyl species can either be lost or gained depending upon which pathway dominates, the time-temperature profile employed in oxidation studies will have a significant effect on the overall composition of the oxidized coal. Commonly employed coal pre-drying procedures prior to oxidation is expected to alter the composition of the final oxidized coal since such pre-drying is similar to the thermal step examined in this work.

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Table I

Analytical data for coals representative of the samples utilized[1]

PARAMETER	ILLINOIS No. 6	RAWHIDE
Rank	HV-C	SBB-C
% Carbon (DMMF)	79.44	73.40
H/C	0.844	0.836
O/C	0.999	0.201
COOH (per 100 carbon)	0.5[2]	3.2[3]
Organic S (DMMF)	3.08	0.93
Phenolic OH (per 100 carbon)	4.5[2]	4.8[3]
Total S (Dry)	3.94	0.92
Pyritic S. (Dry)	1.17	0.01
Mineral Matter	10.94	7.06

1. All analysis (except as noted) are from data from similar samples contained in the Coal Characterization Library of the Exxon Coal Research laboratory, Baytown, Texas. Sample to sample variations are expected as well as differences due to sample preparation. The numbers, therefore, are useful only in addressing trends.

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3. Analyses were kindly provided by Dr. R. Liotta and obtained from samples representative of those utilized.

Fig. 2 - Pyridine adsorbed on Rawhide coal (A) before and (B) after having been subjected to vacuum drying at 100°C. The 3 indicated absorptions are pryidine specific.

Fig. 3 - FT-ir difference spectrum of Illinois No. 6 pretreated by vacuum drying at 100°C and subjected to O_2 treatment at 100°C. Absorption increases of the oxidized coal as compared to the dried (100°C) starting coal are shown.

Fig. 1 - FT-ir difference spectrum of Illinois No. 6 coal subjected to vacuum drying at 100°C showing absorption losses relative to the coal before heating.
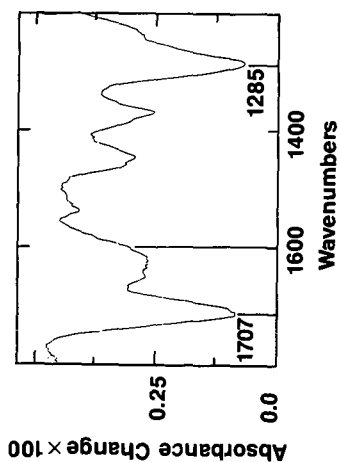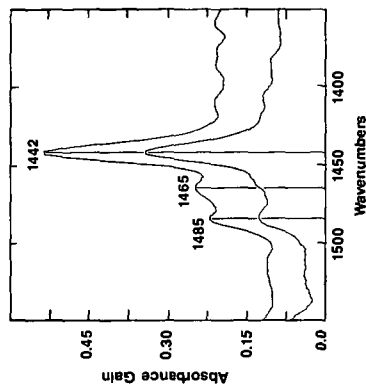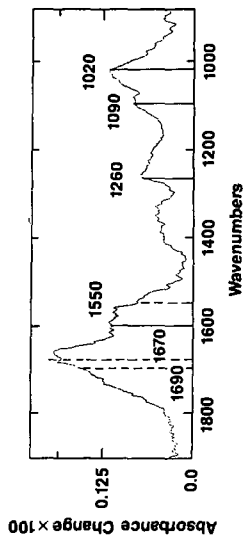
The Structure and Plastic Properties of Coals Following
Low-Temperature Catalytic Hydrogenation

P. G. Stansberry, R. Lin, C. W. Lee, M.-T. Terrer,
F. J. Derbyshire, and A. Davis

College of Earth and Mineral Sciences
The Pennsylvania State University
University Park, PA 16802

Abstract

Following earlier work, studies have been continued in examining the physical and chemical changes which occur in coals following low-temperature ($\leq$ 400°C) catalytic hydrogenation. Reactions were conducted with a series of coals ranging in rank from subbituminous to low volatile bituminous and using a dispersed Mo catalyst in the absence of solvent. With progressive hydrogenation, the yield of extractable liquids substantially increased for all coal samples except the low volatile bituminous coal. There were corresponding increases in the coal fluid properties. Low-temperature hydrogenation was also found to negate the adverse effects of air oxidation on coal fluid behavior.

Although hydrogenation improved coal fluidity, it essentially eradicated any swelling properties of the parent coal. Experiments using blends of hydrogenated coals and hydrogenated coal extracts with parent coals showed that dilatation could be greatly improved for a bituminous coal by the addition of hydrogenated bituminous coal extract. No other blends exhibited swelling properties. It is suggested that the phenomenon of swelling is due to a particular chemical interaction between the mobile liquids (indigenous or extraneous) and the chemical structure of the coal macromolecular network.

Introduction

It has been known for several decades that heating certain coals, at or near their softening point, may result in a several fold increase in the content of extractable liquids (1-8). Furthermore, it has been demonstrated that the fluid properties of the parent coals correlate with the yield of extractable liquids from the heat treated coals (most often when chloroform was used as the extracting solvent) and that both of these characteristics passes through a maximum in coals between 85 to 88% carbon content (5,6,9,10).

The effect of the low molecular weight, hydrogen-rich, chloroform-soluble material on the plastic behavior of coal has been explained by the hypothesis that the development of plasticity is a transient, in-situ, hydrogen-donor process (11). These lighter molecular weight substances not only play an essential role in plasticity development, but also are influential in coal liquefaction (12,13).

A decrease in the yield of extracts (14) and a significant decrease in plastic properties (14,15) can be effected by mild oxidation. Ignasiak et al. (16) have suggested that the incorporation of reactive oxygen groups (as phenolic, acidic, or ketolic oxygen) may act as the agents responsible for the formation of cross-linkages during the heating of the coal, leading to an overall reduction in the internal mobility of the coal molecules. Conversely, hydrogenation of oxidized or high oxygen content coals can result in the development of plastic properties (17-19).

In earlier reported research (13,20), which was directed towards deriving coal structural information through low-severity catalytic coal liquefaction in the

absence of solvent, it was found that, as the yield of extractable liquids increased, the coals became progressively more fluid. Further investigations have since been made of the relationship between the catalytically generated liquids and coal fluid properties for a series of coals of different rank. The findings are presented in this paper.

Experimental

1) Coal Properties and Preparation

The coals studied were obtained from the Pennsylvania State Coal Sample Bank and were selected to cover a range of rank from subbituminous to low volatile bituminous; each containing over 80% vitrinite. Properties of the coals are shown in Table 1.

The coals were ground to -20 mesh under conditions to minimize oxidation and were subsequently stored under nitrogen and used without drying. For catalytic hydrogenation experiments, the coals were impregnated with 1% wt (dmmf) Mo by slurrying with an aqueous solution of ammonium tetrathiomolybdate. After slurrying, the excess water was removed by drying under vacuum below $100^{\circ}C$.

A high fluidity coal (PSOC-1296) was chosen for studies to examine the effects of oxidation on plastic properties. The coal was oxidized under mild conditions by passing air through a bed of the finely ground coal (-40 mesh) at $50^{\circ}C$ for four days.

2) Catalytic Hydrogenation

Hydrogenation reactions were conducted in tubing bomb reactors under an initial (cold) hydrogen pressure of 7 MPa and at temperatures between 250 and $400^{\circ}C$ for times of 5 to 60 min. The yields of light gases were determined by volumetric measurement and gas chromatographic analysis.

In some cases, the reacted coals were extracted in chloroform, using a Soxhlet apparatus, to obtain a partition into soluble extract and residue. More detailed descriptions of the experimental procedures have been reported (13,20,21).

3) Analytical

The fluid properties of coals, hydrogenated coals and blends of coals with coal extracts were studied using an automated Gieseler plastometer, following the ASTM standard procedure (22), and a pressure microdilatometer. The latter was operated at a heating rate of $20^{\circ}C$ min^{-1} from ambient under 0.1 MPa of nitrogen.

Results and Discussion

The yields of gases and chloroform-soluble extract obtained upon catalytic hydrogenation of the coals for 60 min at 350 and $400^{\circ}C$ are given in Table 2. Reaction at $350^{\circ}C$ caused a significant increase in the yields of chloroform-soluble extract over that obtained from the parent coal, the greatest response being obtained with the subbituminous coal, PSOC-1403. This observation is consistent with reported data showing that, under these reaction conditions, low-rank coals were more reactive than bituminous coals (13). At $400^{\circ}C$, high extract yields were obtained with all of the coals except the low volatile bituminous coal, PSOC-1325. It is supposed that the structure of a coal at this stage of metamorphism contains such a high proportion of strong covalent bonds that it is difficult to break down into lower molecular weight species, even in the presence of an active catalyst.

Mild oxidative treatment of the hvA bituminous coal, PSOC-1296, reduced the yield of extractable liquids, a commonly observed phenomenon. However, the subsequent catalytic hydrogenation of this coal appeared to have more than counteracted the effects of oxidation.

The results of Gieseler plastometer measurements on catalytically hydrogenated and unextracted coals are shown in Figures 1(a) - (c). The effect of reaction time on the fluidity of an hvA coal can be seen in Figure 1(a). With increasing reaction time at 400°C, which corresponds to a progressive increase in the content of extractable liquids, the coal softening temperature was lowered and the maximum fluidity was increased. For times longer than 15 min, the maximum fluidity exceeded the measurable range of the instrument. Similarly, reaction for 60 min at 400°C introduced fluid behavior to subbituminous coals which, in their parent state, produced no response in the Gieseler plastometer, Figure 1(b).

In parallel with the measured effects of oxidation of the hvA bituminous coal in lowering the yield of chloroform-extractable liquids, the fluid properties were also suppressed, Figure 1(c). Catalytic hydrogenation of the oxidized coal was instrumental in increasing the fluidity above that of the original coal.

The development of fluidity in these coals, as measured by the Gieseler plastometer, is not to be confused with the swelling behavior shown by coking coals. Examination of the treated coals in the microdilatometer showed that, consistent with the Gieseler measurements, the coal softening temperature had been reduced. However, all of the samples underwent a volume contraction with increasing temperature, even those which had exhibited a net volume expansion or dilatation prior to treatment. These results were interpreted to mean that the catalytic hydrogenation had increased the coal fluidity to such an extent that, in the melted state, the viscosity was so reduced that volatile pyrolysis products could freely escape without causing the coal to swell. In effect, the volume contraction meant that, upon becoming fluid, the density of the coal sample had increased.

A number of experiments were then conducted, using a bituminous and a subbituminous coal (PSOC-1266 and PSOC-1403, respectively) to determine whether blending the hydrogenated products with untreated coals could influence swelling behavior. Mixtures of unextracted hydrogenated coals with the parent coal, in which the concentration of the former was increased up to 50% wt did not appreciably influence the swelling behavior of either coal, although, for the bituminous coal, there was a steady reduction in softening temperature with increasing concentration of the treated coal.

Blending the extract from the hydrogenated bituminous coal with the parent coal had a dramatic effect upon swelling properties, Table 3. This effect was not found with any other combination of the parent bituminous or subbituminous coal with either extract from the hydrogenated coals, although blending did reduce the initial softening temperature and increase the volume contraction in each case.

It is assumed that the extracts from the hydrogenated coals and in particular the bituminous coal will contain a reasonable proportion of hydroaromatic structures. The presence of H-donor compounds is thought to enhance the plastic behavior of coals (11). The results presented here suggest that the phenomenon of swelling is attributable to a particular combination of (possibly) H-donor properties of the mobile liquids within coals (and added liquids such as the extract from the hydrogenated bituminous coal) together with the structural configuration of the coal macromolecular network.

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TABLE 1

COAL PROPERTIES

Penn State Sample Bank Number	PSOC-1325	PSOC-1296	PSOC-1022	PSOC-1266	PSOC-1403	PSOC-1414
Seam	L. Kittanning	L. Kittanning	L. Kittanning	L. Kittanning	Anderson	Beulah-zap
County	Somerset	Armstrong	Lawrence	Mahoning	Campbell	Mercer
State	Pennsylvania	Pennsylvania	Pennsylvania	Ohio	Wyoming	N. Dakota
ASTM	LV	HVA	HVA	HVA	SUBBT B	SUBBIT C
Mean-Maximum Reflectance of Vitrinite (Romax, %)	1.63	0.87	0.80	0.83	0.40	no data
Moisture Content (a.r. % wt)	1.2	1.1	3.8	3.4	17.8	25.4
Mineral Matter (dry, % wt)	13.5	20.3	17.2	6.1	11.9	10.8
Elemental Composition (% dmmf)						
Carbon	90.0	85.7	82.9	83.2	73.0	71.0
Hydrogen	5.0	5.5	5.7	5.0	4.5	6.6
Oxygen	2.8	5.8	7.7	8.6	20.4	21.1
Nitrogen	1.6	1.5	1.6	2.1	1.2	0.7
Organic Sulfur	0.6	1.4	0.6	0.5	0.9	0.6
Petrographic Composition (mineral-free, % vol)						
Vitrinite	96	88	81	91	87	83
Exinite	0	2	13	3	2	2
Inertinite	4	10	6	6	11	15

TABLE 2

YIELDS OF GASES AND CHLOROFORM-SOLUBLE EXTRACT (% dmmf) FROM CATALYTICALLY HYDROGENATED COALS

(1% wt Mo (dmmf); no solvent; 60 min reaction; 7 MPa cold H_2 pressure)

Coal	ASTM Rank	CHCl₃ Extract for raw coal	Reaction Temperature (°C)					
			350			400		
			CHCl₃-solubles	CO_x	C_1-C_4	CHCl₃ solubles	CO_x	C_1-C_4
PSOC-1325	lvB	0.6	12.9	0.2	0.4	12.8	0.1	0.7
PSOC-1266	hvA	0.9	8.8	0.2	0.0	59.1	0.3	0.8
PSOC-1022	hvA	2.5	13.3	0.7	0.3	54.3	1.8	1.5
PSOC-1296	hvA	5.0	--	-	-	49.6	0.5	0.8
PSOC-1403	Sub. B	4.3	33.4	7.2	0.8	52.3	12.4	4.0
PSOC-1414	Sub. C	2.3	--	-	-	37.0	17.2	4.1
*PSOC-1296	hvA	0.6	--	-	-	54.5	1.3	4.1

*Pre-oxidized coal

TABLE 3

DILATOMETRIC PARAMETERS FOR MIXTURES OF BITUMINOUS COAL (PSOC 1266)
WITH THE CHLOROFORM-SOLUBLE EXTRACT OF THE HYDROGENATED COAL

wt% hydrogenated extract in mixture	0	5	10	20
Softening temperature, °C	435	410	395	367
Temperature of maximum contraction, °C	477	460	450	435
Temperature of maximum expansion, °C	500	487	480	485
Resolidification temperature, °C	---	---	500	495
% maximum volume* contraction	21	24	21	26
% maximum volume* expansion (net)	23	52	129	349
% volume expansion* on resolidification (net)	---	---	80	349

*measured relative to original coal volume

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**Fluidity Change with Progressive
Catalytic Hydrogenation (400°C)**

60 min

30 min

15 min

Parent
Coal

Temperature °C

Coal: PSOC–1266, hvA

(a)

**Fluidity of Subbituminous Coals Catalytically Hydrogenated
at 400°C (Parent coals have no fluidity.)**

Giesler Fluidity, DDPM

PSOC–
1414

PSOC–
1403

Temperature °C

(b)

**Effects of Mild Oxidation and Subsequent Catalytic
Hydrogenation on Coal Fluidity**

Parent
Coal

Oxidized Coal
following catalytic
hydrogenation

Oxidized
Coal

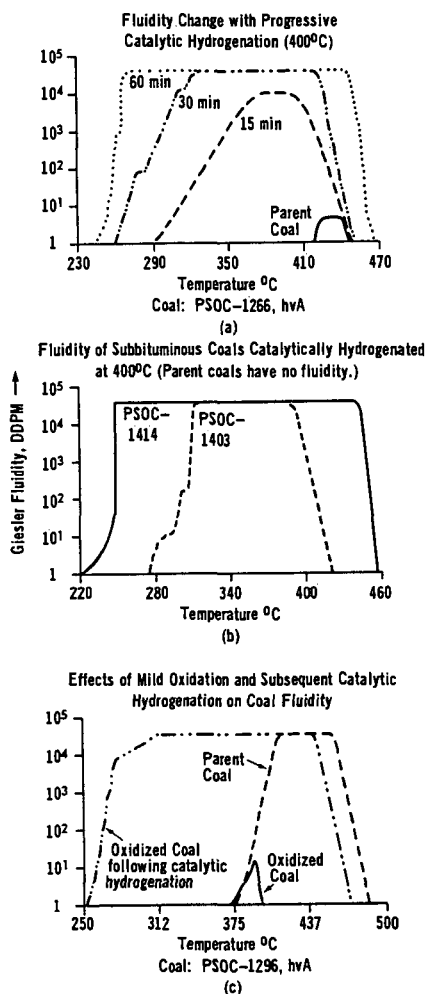Temperature °C

Coal: PSOC–1296, hvA

(c)

**Figure 1. GIESELER PLASTOMETRY MEASUREMENTS OF HYDROGENATED
AND PARENT COALS**

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DISTRIBUTION OF IMPREGNATED METAL HALIDE CATALYSTS IN COAL GRAINS

David M. Bodily and Jyi-Perng Wann

Department of Fuels Engineering, University of Utah
Salt Lake City, Utah 84124

INTRODUCTION

Metal halides such as stannous chloride and zinc chloride are known to be effective coal hydrogenolysis catalysts (1-3). Weller et al. (1) examined a number of potential catalysts and found zinc and tin chlorides to be among the best. Although stannous chloride is generally recognized to be more active than zinc chloride, zinc chloride has been chosen as the catalyst in a number of coal liquefaction systems. These include processes developed in Japan (4), molten salt reactors (2,3) and short residence time reactors (5-7).

The metal halides appear to be active in cleaving bridges between groups of condensed aromatic rings (unit structures) under liquefaction conditions. This results in a progressive depolymerization of the coal, ultimately to isolated unit structures, with little reaction of the condensed ring systems themselves (8-10). This results is less hydrogen consumption and a soluble product that can be further upgraded. Weller et al. (1) suggested that a metal sulfide was formed, which was the active catalytic species. Zielke et al. (2) proposed a complex of zinc chloride and water to form a Friedel-Crafts type acid, for the case of zinc chloride catalyzed liquefaction. Bell and coworkers (11-14) studied the cleavage in model compounds with ether and carbon-carbon bonds, species that are thought to form bridges between unit structures in coal. They proposed a similar active species. This conclusion was supported by a study of Beishline et al. (15). The hydrogenolysis reaction begins at the surface of coal grains and proceeds towards the center (16,17). As the bridges are broken, the coal softens and reacts. The metal halides lower the temperature at which the coal softens (18) and also the temperature at which the exothermic coal hydrogenation reaction occurs (19).

Contacting of the metal halide with the bridging structures is required for the liquefaction reaction to proceed. At the temperatures of liquefaction processes, the coal softens and both thermal and catalytic bond cleavage occurs. The reactions are rapid, but may lead to retrogressive reactions if sources of hydrogen are insufficient or the catalyst is not present (20,21). The semi-coke formed by the retrogressive reactions is less reactive to liquefaction and increases the reaction time and severity of conditions required for high conversions. Partial liquefaction under hydrogen deficient conditions may induce sufficient fluidity for mesophase to form. Recently, the liquefaction of coal at mild conditions, below the normal softening temperature, has been studied (22). The process involves two steps: hydrotreating of metal halide impregnated coal and base catalyzed depolymerization of the products. The temperature of the process is kept below 275°C. Under these conditions, the fluidity of the system is low and it is important to have good contact between the metal halide catalyst and the bridges that are to be cleaved. The catalytic reactions must occur and the thermal reactions must be suppressed. It is therefore important that a good dispersion of the catalyst throughout the coal grains be achieved.. The effect of impregnation method on the dispersion of the catalyst is the subject of this report.

EXPERIMENTAL

Four coal samples were studied in these experiments. The ultimate analysis of the coals is shown in table 1. The preparation of the samples for analysis is shown schematically in figure 1. The coals were ground to -60/+100 mesh and extracted with THF in a Soxhlet extractor. Some samples used for X-ray analysis were demineralized by HCl and HF. Water, acetone and methanol were used as solvents for impregnation of the metal halides. Reagent grade $ZnCl_2$, $FeCl_3$, $NiCl_2 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$ and $SnCl_4 \cdot 5H_2O$ were impregnated on the coals. The solvent, metal halide and coal were mixed in the desired amounts. The mixture was stirred and agitated in an ultrasonic bath for two hours. The coal/metal halide mixture was then dried to remove the solvent.

Grain mounts were prepared with epoxy mounting medium, ground and polished to expose cross sections of the coal grains. A Hitachi (model S-500) scanning electron microscope was used to examine the samples. The electron energy was 20,000 KeV. A Kevex energy-dispersive spectrometer was used to map fluorescent X-rays from the metal atoms and the chlorine. X-ray diffraction was used to measure changes in the spacing of clusters of condensed-ring aromatic groups. The assignment of X-ray diffraction peaks was by comparison with the diffraction pattern of graphite.

RESULTS AND DISCUSSION

Polished grain mounts of the metal halide-impregnated coal samples were examined with the scanning electron microscope. Grinding and polishing of the grain mounts exposes a cross section of the coal grains. Fluorescent X-rays, emitted from the surface of the mount, were measured with the energy dispersive detector as the sample was scanned. A narrow band of X-rays, corresponding to a specific atom, were recorded on photographic film as the sample was scanned. The distribution of the given atom in the coal grain was thus obtained. The metal atom and chlorine atom distributions for various impregnation conditions were determined. If the metal halide is uniformly distributed throughout the coal grain, the photograph will show a uniform exposure throughout the cross section of the coal grain. If the metal halide is poorly distributed throughout the coal grain, the photograph will show exposure at the edge of the cross section and along cracks, but not in the center of the grains. Some background exposure will be seen in areas where the epoxy mounting medium is exposed at the surface. Electron micrographs of the coal grains were also obtained. The X-rays mostly originate near the surface, since the depth of penetration of the electrons is not great.

The distribution of the metal halides within coal grains is qualitatively shown in figure 2. The interpretation is subjective and is based on observation of several grains for each sample. Good dispersion of the metal halides is achieved with organic solvents. Both methanol and acetone are effective in dispersing the metal halides and under the conditions of these experiments, it is impossible to determine if one is better than the other. Both of these solvents are known to swell coals. Stannous chloride is the most easily dispersed of the metal halides tested. Nickel and iron chlorides are more difficult to disperse from aqueous solution. The effectiveness of dispersion of the metal halides varies with the coal samples, but does not follow rank.

Beall (23,24) has reported the possible formation of intercalation compounds of coal with the chlorides of iron, chromium, and copper at temperatures from 215°C to 150°C. The formation of intercalates has been suggested as a possible mechanism in the catalysis of coal hydrogenolysis by metal halides. The possible formation of intercalates was investigated by X-ray diffraction of the impregnated samples. Formation of an intercalation complex would be expected to shift the 002 diffraction peak, corresponding to a larger interplanar spacing in the clusters of condensed-ring aromatic groups. Demineralized samples were studied to remove the interference from diffraction peaks due to mineral matter. Impregnation of metal halides decreased the intensity of 002 diffraction peaks due to scattering of X-rays by the metal atoms, but the peaks were not shifted. Although the formation of intercalates cannot be ruled out by these experiments, there is no evidence to support intercalate formation.

Acetone and methanol swell coals and are also effective in impregnating metal halides throughout the coal structure. Examination of swollen coals, from which the solvent has been removed, by X-ray diffraction show no changes in the 002 diffraction peak. The solvent is apparently imbibed by the amorphous regions surrounding the clusters of condensed-ring aromatic units, but does not disrupt the clusters. The metal halides appear to be deposited in these amorphous regions as the solvent is evaporated. Water does not swell coal, but it is adsorbed on coal surfaces within pores. Impregnation from aqueous solution is not as effective as from organic solution and depends strongly on the coal and the metal halide properties. Impregnation of stannous chloride from aqueous solution at room temperature can be quite effective in achieving high dispersion at the microscopic level, which is the limit of resolution of these techniques. The dispersion at the molecular level for impregnation from either aqueous or organic solutions cannot be measured by these procedures.

CONCLUSIONS

Impregnation of metal halides throughout coal structures is more effective from organic solutions than from aqueous solutions. High dispersion of the metal halide is attributed to the ability of the solvent to penetrate the coal structure and cause swelling. A minimum solubility of the metal halide in the solvent is also required. No evidence for the formation of intercalation compounds between the metal halides and condensed-ring aromatic structures in the coal has been found.

Good dispersion of potential coal hydrogenolysis catalysts throughout the coal is expected to be important in low-severity coal liquefaction processes. Liquefaction may be expected to be achieved below the normal softening temperature of the coal. Good dispersion may also prevent the formation of less-reactive semicoke during liquefaction at higher temperatures. Under conditions of good catalyst dispersion and hydrogen accessibility, depolymerization of coal to soluble products may be expected to occur rapidly.

ACKNOWLEDGMENTS

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Table 1. Ultimate Analysis of Coal Samples

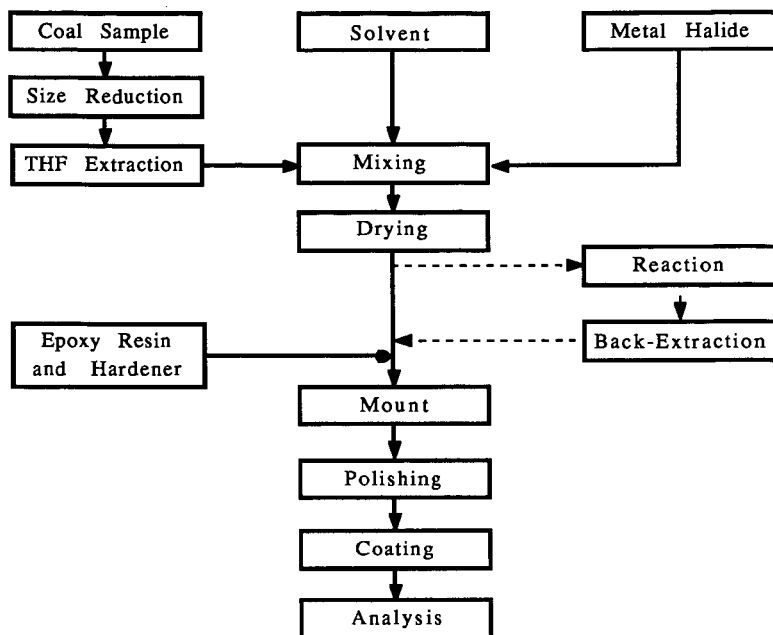|	Wyodak	Burning Star	Elkhorn	Coal Basin
Carbon, %	76.0	78.9	85.4	90.3
Hydrogen, %	5.4	5.4	5.1	5.4
Nitrogen, %	1.4	1.2	1.8	2.2
Sulfur, %	0.6	4.4	0.7	0.7
Oxygen, % (dif)	16.6	10.1	7.0	1.4

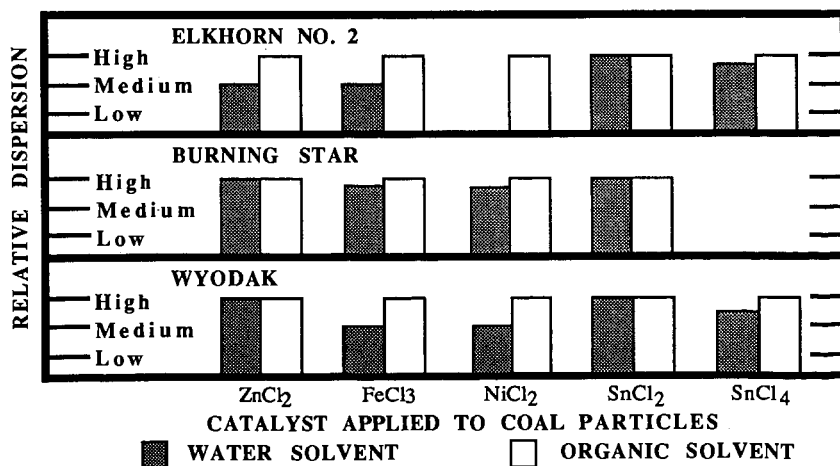Figure 1. Flowchart for SEM Mount Preparation

Figure 2. Catalyst Dispersion

A PSEUDOKINETIC STUDY OF COAL LIQUEFACTION

D.H. Finseth, B.C. Bockrath,
E.G. Illig, and B.M. Thames
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

All approaches to the study of the chemistry of coal liquefaction are handicapped to one degree or another by the inability to accurately measure the detailed structure of the primary reagent of interest -- coal. Recent work at PETC has focused on utilizing quantitative ^{13}C NMR together with elemental balances to obtain an improved picture of the molecular level chemistry of hydrogen in realistic conversion environments. The method divides total hydrogen incorporated into the organic products into that consumed in hydrogenation, heteroatom removal, and hydrogenolysis. The details of this approach have recently been discussed [1]. To date, the approach has proven useful in describing the influence of reaction temperature [1,2] and catalyst [3] on the utilization of hydrogen. This work describes efforts to determine the relative rates of hydrogen-consuming reactions -- hydrogenolysis, hydrogenation, and heteroatom removal.

Experimental

All reactions were done on a shaking microautoclave system, which has the capacity to simultaneously immerse five 40 milliliter microreactors into a preheated fluidized-bed sandbath. This system has a heat-up time of approximately 5 minutes. Prior to reaction the microreactors were charged with 4 g of Illinois No. 6 hvC (River King) bituminous coal and 7 g of a heavy coal-derived distillate (240°C-450°C cut from the SRC-II Process), and pressurized to 1200 psig with hydrogen at ambient temperature. This loading procedure results in a hydrogen pressure of approximately 2000 psig at reaction temperature. Catalytic runs were accomplished by loading the coal with 0.006 g of either molybdenum (as ammonium heptamolybdate) or tin (as $SnCl_4$). Reactions were run at 0-, 5-, 10-, 20-, 30-, and 60-minute reaction times (time at 380°C).

Following reaction the headspace gas was quantitatively collected and analyzed by gas chromatography. The total reaction product was removed to a Soxhlet thimble and separated via CH_2Cl_2 extraction into soluble and insoluble fractions. Both product fractions were analyzed for elemental composition via microanalytical procedures by Huffman Laboratories.

Both ^{13}C and ^{1}H high-resolution NMR spectra were obtained in CD_2Cl_2 on the soluble fractions using a Varian XL-100 spectrometer. The ^{13}C NMR

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spectra of the feed coal and the CH_2Cl_2 insolubles were obtained via crossed polarization magic angle spinning, CP/MAS, techniques using a Brücker CXP-100 instrument.

Results and Discussion

The hydrogen utilization profiling method involves measurement of the ^{13}C NMR aromaticity change during reaction as a direct quantitative measure of the degree of hydrogenation of the feed slurry. The total hydrogen incorporation is obtained from the elemental analysis, and the amount incorporated in heteroatom removal is estimated from the change in organic heteroatom content. In these low-temperature reactions ($380^{O}C$), negligible amounts of light hydrocarbon gases were produced. Thus any hydrogenolysis observed must involve cleavage of slurry matrix bonds to yield smaller solid and liquid fragments. It must be remembered that because there is no means of counting bonds, the amount of hydrogen incorporated via hydrogenolysis must be obtained by difference:

Total hydrogen - (hydrogenation + heteroatom removal) = hydrogenolysis.

The data in final form are simply the number of hydrogens, per 100 carbons of feed slurry, that are incorporated into organic products via hydro-genation, heteroatom removal, and hydrogenolysis (bond cleavage) reactions.

The results of this study of hydrogen utilization are presented in Figure 1. Figure 1a shows the total net hydrogen incorporation into organic products as a function of time for uncatalyzed and tin- and molybdenum-catalyzed reactions. The catalyzed systems appear to incorporate hydrogen more rapidly than the uncatalyzed reactions (note 20- and 30-minute reaction times), but at the longest reaction time (60 minutes), there is no dif-ference between the total net hydrogen incorporation in catalyzed and uncatalyzed reactions. For the catalyzed reactions the results suggest that product hydrogen content actually decreases from 30 to 60 minutes, whereas in the noncatalyzed reaction, hydrogen is still being incorporated during this time period. This may indicate that retrogressive reactions are important at longer reaction times in the catalyzed reactions. Analysis of headspace gas composition after reaction indicates that this decrease in hydrogen content is not due to hydrogen starvation. The behavior shown in Figure 1 at short reaction times, ≤ 10 minutes, is seemingly erratic. How-ever, it does suggest that in general the chemistry is different, either in rate or in the nature of the reactions, from that observed at longer reaction times.

The data in Figure 1b indicate that there is essentially no dependence of heteroatom removal on either catalyst addition or reaction time under these conditions.

The amount of hydrogen incorporated into products via hydrogenation reactions is measured directly by measuring the change in aromaticity during reaction. The data obtained for incorporation of hydrogen by hydrogenation are presented in Figure 1c. It first must be stressed that optimistic error limits on measurement of the change in aromaticity, Δf_a, are ± 0.02. This error translates directly into an error of ± 2 hydrogens per 100 carbons.

With this caution, the data in Figure 1c indicate no significant change in degree of hydrogenation with reaction time. However, it is intriguing to note that all three sets of data -- molybdenum-catalyzed, tin-catalyzed, and uncatalyzed -- show evidence of hydrogenation at 10-minute reaction times and show a drop in the degree of hydrogenation between 10 and 20 minutes. Both catalytic runs also exhibit slightly higher levels of hydrogenation than the noncatalyzed reaction from 20 minutes to 60 minutes of reaction. These small differences are within the limits of error of the method.

The most difficult (and error-prone) mode of hydrogen utilization to measure is the hydrogen incorporated into the system via hydrogenolysis or bond cleavage chemistry. This mode of utilization is determined by difference and incorporates the sum of the errors of the other analyses (total hydrogen, heteroatom removal, and hydrogenation). With this qualification, the data that describe hydrogen incorporation in bond cleavage chemistry are very interesting (see Figure 1d). They indicate that for the first 10 minutes of reaction, there is progressively more net bond formation (condensation). This is followed by a period, 10-30 minutes, during which bond cleavage predominates. Both catalytic systems appear to reach their peak in hydrogenolysis consumption at 30 minutes under these conditions. This maximum is followed by a slight decrease in net hydrogenolysis on going to 60-minute reaction times. The data in Figure 1d suggest the existence of a sequential mechanism for conversion under these conditions. At short reaction times, the apparent internal hydrogen redistribution is based on condensation (bond-making) chemistry, while at longer reaction times, bond cleavage (hydrogenolysis) chemistry appears to predominate.

The hydrogen utilization profile data in Figure 1 can be contrasted with the conversion data shown in Figure 2. The conversion data were obtained on samples generated under conditions identical to those used for generation of Figure 1. Neither of these solubility-based conversion plots seem consistent with the hydrogen utilization data, particularly at short reaction times. The solubility data do not indicate any substantial effect of added catalyst and show no apparent qualitative differences between short reaction times and long reaction times. In particular, the time dependence of conversion based on solubility in the two solvents appears to be substantially different. The THF solubility shows an abrupt change at short reaction time, while cyclohexane solubility is essentially a linear function of reaction time. This lack of correspondence between solubility-based conversion values and hydrogen utilization profiles is probably an indication that the two techniques are measuring different properties of the liquefaction system. It seems likely that solubility, especially in strong solvent systems, might be sensitive to physical changes in the system that are not probed by the chemical methods used in hydrogen utilization profiling. It is possible that the hydrogen utilization profile approach may prove to be more useful in investigations of the detailed chemical mechanism of liquefaction.

Conclusions

The hydrogen utilization profiles as a function of reaction time indicate that two different time regimes of reactivity may exist under these mild reaction conditions. At short reaction time the data suggest that

hydrogenation and condensation reactions are operative with minimal net hydrogen incorporation. (The possibility exists that the hydrogen generated in condensation during this time period is being shuttled into more reactive regions of the slurry via hydrogenation). After this initial period of hydrogen redistribution, the major chemistry appears to be bond breaking (hydrogenolysis) that results in significant net hydrogen incorporation into the slurry. This description is consistent with a set of two sequential reactions being responsible for liquefaction under these conditions. The data in this study clearly indicate that both tin and molybdenum accelerate the incorporation of hydrogen into the reacting slurry and imply that the major net effect of the catalysts is to make hydrogen more readily available for hydrogenolysis reactions.

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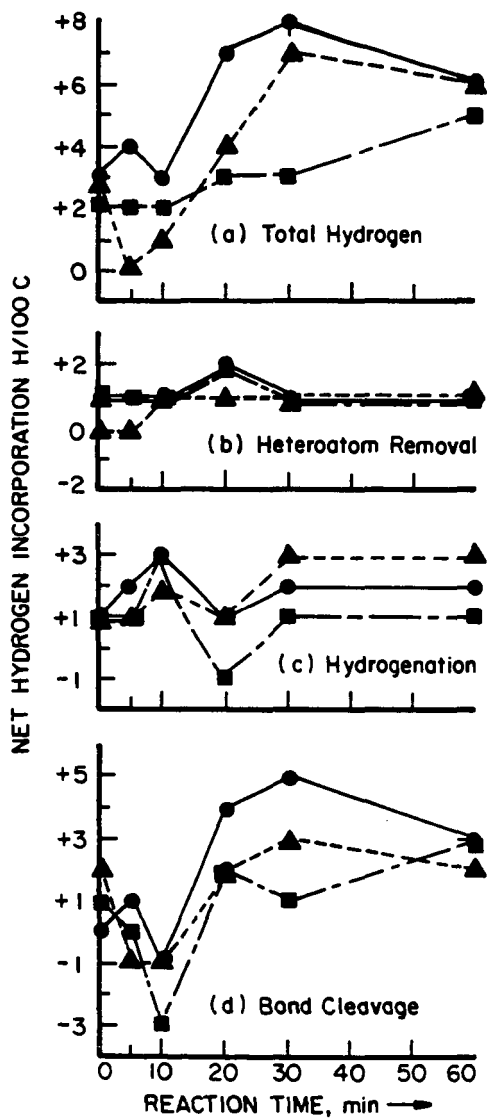
Figure I - Hydrogen Utilization as a
Function of Reaction Time.

● ———— Sn Catalyzed
■ ------ Mo Catalyzed
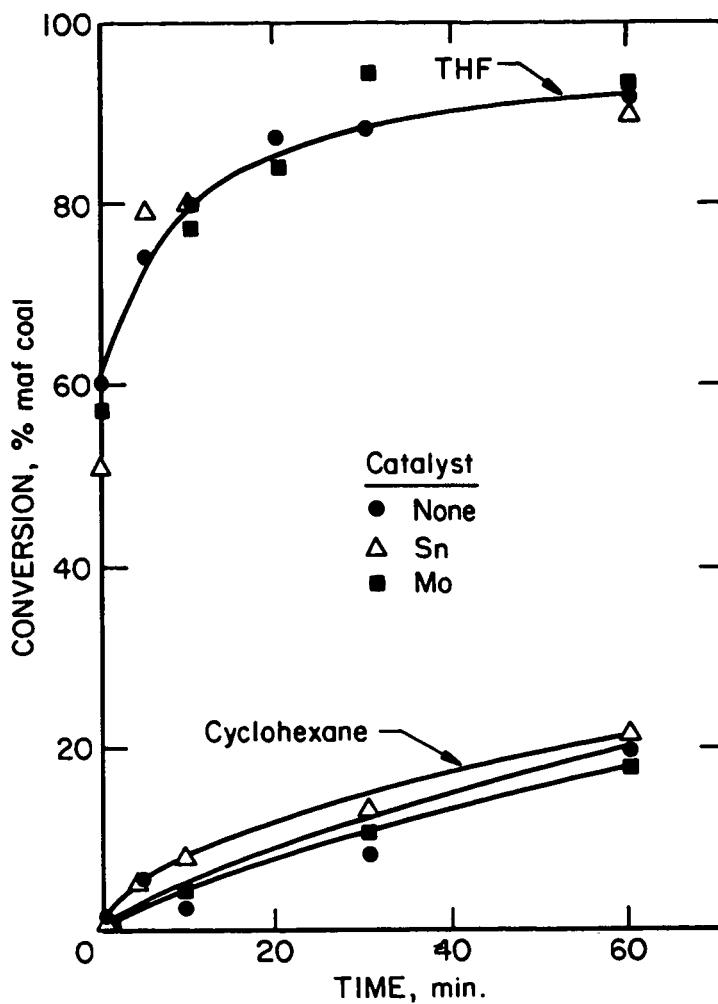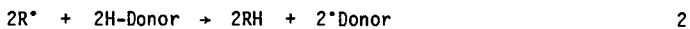▲ —·—·— Uncatalyzed

B&R/10,858

Figure 2 – Conversion of Illinois No. 6 coal at 380 °C.

An Electron Spin Resonance Investigation of Free Radicals
in Lignite Formed Using Programmed Temperatures, H_2S, CO and H_2

Jan Nowok and Virgil I. Stenberg
Department of Chemistry, University of North Dakota
Grand Forks, North Dakota 58202, USA

INTRODUCTION

The conversion of low-rank coal to liquid products has traditionally been performed in organic donor solvents at constant reactor temperatures. In one view of coal liquefaction, the thermolysis of weak bonds in the coal structure is followed by H transfer to the coal-derived radicals by hydrogenation atom donor molecules, reactions 1 and 2. To minimize adduction and allow organic

$$\text{coal-coal} \rightarrow 2R^{\bullet} \qquad\qquad\qquad \underline{1}$$

$$2R^{\bullet} + 2\text{H-Donor} \rightarrow 2RH + 2^{\bullet}\text{Donor} \qquad\qquad \underline{2}$$

materials to enter the product stream, we have recently developed a new donor solvent, H_2O-H_2S with CO and H_2, as a substitute for the organic slurrying solvent (1,2) and reducing gases. For ZAP lignite, volatile product conversion for the reaction performed in H_2O-H_2S-H_2-CO at 420°C is 42.8%; and, for H_2O-H_2-CO, it is 37.4% (1). Our current research into the chemistry of liquefaction has yielded considerable progress using the linear temperature programmed reactions, 300-500°C. The conversion to volatile products using by H_2O-H_2S-H_2-CO is equal 59.3% (3).

A number of investigators have applied ESR to examine radicals formed during pyrolysis of coal (4-11). Since the method of electron resonance is a very sensitive, we have chosen this technique to investigate mutual interactions of coal-derived radicals with reducing gases.

EXPERIMENTAL

The ZAP lignite (Table 1) was ground to less than 37 μm. About 30-50 mg of lignite sample was inserted in a 2 mm i.d. Pyrex tube together with 20-30 mg of glass wool. The samples were dried in vacuum 1 Torr at 50°C for 3 hrs. The liquefaction was performed under reducing gases using the linear programmed temperature range of 300-500°C over the period of 1 hr in the batch autoclaves.

When the temperature 500°C was reached, the reactors were vented to remove oil and gas, cooled down in water (20°C) and next in ice.. The samples were immediately sealed under argon, and the ESR measurements were carried out within 10-15 min at room temperature. According to Petrakis (12), upon cooling to room temperature, spin concentrations in coal are, in general, the same as at the high temperature. The spin concentrations and g values were determined by the sample interchange method. DPPH was employed as the standard. Spin concentrations were calculated on final and initial amounts of lignite. The spin concentration (SC) data was employed to calculate the conversion to distillate products by using the equation 3. The calculated conversion (SC)

$$\% \ \text{conversion (SC)} \ = \ \frac{\text{SC(final)} - \text{SC(initial)}}{\text{SC(final)}} \ x \ 100\% \qquad \underline{3}$$

has been correlated with similar conversion values into volatile products independently determined by employing the traditional techniques (1).

All ESR spectra were recorded using a Brucker ER-420 spectrometer. Duplicate samples were prepared for all different sets of liquefaction conditions to check reproducibility.

RESULTS AND DISCUSSION

(a) The effect of H_2S on stabilization of coal-derived radicals

The typical ESR spectrum of a ZAP lignite sample is a single symmetric signal without hyperfine structure (Figure 1). This signal is distinguishable by it's g-value, linewidth and spins g^{-1}. For unreacted coal, they are 2.0021, 8.3 G and 1.8×10^{19} spins g^{-1}, and for pyrolyzed coal linear programmed over 300-500°C for 1 hr, the values are 2.0011, 6.8 G and $20.2 \pm 1.9 \times 10^{19}$ g spins g^{-1}, respectively. Decreases in ESR g value is known to be a consequence of the evolution of heteroatom-containing gases such as CO_2 and H_2O which are formed during the pyrolyses (13). The decrease in linewidth of the sample can be attributed to the dehydrogenation reactions known to be occurring concurrently.

A representative spectrum of ZAP lignite which has been reacted with H_2S is reproduced in Figure 2. This spectrum consists of two symmetric signals:

one is positive (+) and one is negative (-). The positive signal can be attributed to coal-derived and some organo-sulfur radicals. It is close to Lorentzian in shape. The observed negative curve has a Gaussian shape, and it represents radicals associated a variety of, organo-sulfur bonds. The existence of the negative signal suggests an altered magnetic environment of these unpaired electrons.

More recent measurements of the ^{33}S hyperfine structure have revealed three basic forms of sulfide radicals: $RCH_2S^{\cdot}$, $RCH_2SS^{\cdot}$ and $(RCH_2SSCH_2)^-$ (14). The g tensor, which has proven to be widely applicable for identification of sulfur-centered radicals, does not provide a critical distinction between the monosulfide and disulfide forms of these radicals. There seems to be agreement (15) that the disulfide radical anion forms from $RS^{\cdot}$ by reaction 4. The

$$RS^{\cdot} \; + \; RS^- \; \rightleftharpoons \; RSSR^- \qquad\qquad \underline{4}$$

unpaired electron is weakly bounded to the $S \dot{=} S$ $\sigma_{3p}{}^*$ antibonding molecular orbital since it contains a major $3p \leftarrow 3p$ element. The disulfide radical anions can be protonated (16) to give I.

RCH₂   H
  \   /
   S╫╫S
      \
      CH₂R
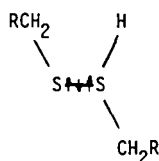
      I

This molecule still has the unpaired electron in the $S \dot{=} S$ $\sigma_{3p}{}^*$ orbital. The S-S bond will probably be weaker than that of the anion.

In this system, one can expect the diffusion of H_2S inward in the coal particle during the heating. This may cause production several kinds of organo-sulfur bonds which can vary with different concentration of H_2S. It is reasonable to assume that charged organo-disulfide radicals can be also formed

in the interior of coal's grain and be distributed as paramagnetic impurities partly stabilized by environment.

By computer analysis of the spectra, it was possible to separate experimental ESR curve into two component spectra. The positive one belongs primarily to coal-derived radicals (positive) and the other to organo-disulfur radicals.

The relationship of spin concentrations per gram to the pressure of H_2S is shown in Figure 3. The lines assigned as I and II were determined by the division of the spin concentration values by the amount of charged lignite and recovered solid material from the reactor, respectively. There is a significant rise of spin density with increasing concentrations of H_2S. The differences in spin concentrations between the two plots I and II represents the amount of coal-derived radicals which have been converted to oil and gas. The line described as theoretical has been calculated from the computer separated signals, and represents the total number of radicals.

The variation of g-value with pressure of H_2S is presented in Figure 4. The g values increase significantly with H_2S pressure. It is related to the amount of heteroatoms incorporated (23). Thiophenolic forms like phenolic forms are effective at causing g-shifts (11).

Figure 5 shows the variation of the ESR line width (ΔH_{pp}) as a function of H_2S pressure. Overall the principal contributor to the positive signal is coal-derived radicals, $\Delta H_{pp} \cong 5$ G and for signal (-) some kind of organo-disulfur compounds $\Delta H_{pp} > 15$ G. The results indicate that hydrogen content in the coal radicals is unchanged with pressure of H_2S. For organo-disulfur compounds, the linewidths fall within the range 14.1-16.6 G with increasing of H_2S pressure. This suggests that other effects may also influence on the ESR linewidth such as electron-proton interactions (13).

It is worthwhile to note that negative ESR signal disappears when previously sulfurized ZAP lignite is exposed to H_2 or CO atmospheres at 500°C. The g-values and linewidths concomitantly decrease to 2.0016 and 5.8 G, respectively.

(b) Effect of H$_2$S and H$_2$ (CO) on hydrogenation of coal-derived radicals.

In H$_2$S-H$_2$ or H$_2$S-CO atmospheres significant differences occur in ESR spectra of ZAP lignite programmed 300-500°C (Figure 6). The line shape varies and is characterized by the disappearance of the negative signal (Figure 2) and the appearance of a narrow peak with a short width of line $\sim$ 1 G. The spin concentration in H$_2$S-CO atmosphere is lower than in H$_2$S-H$_2$ (Figure 7). Therefore, CO decreases the probability of the carbon sulfur bonds formation.

The g values of the ZAP lignite in H$_2$S-CO also changes upon the introduction of H$_2$ particularly at lower pressures of H$_2$S (Figure 8). In the higher fractional pressure of CO ($\approx$ 0.7) in the mixture of H$_2$S + CO there appears, first of all, to be CO interaction with coal radicals. This is mostly pronounced in reaction CO alone with coal radicals (Table 1), g = 2.0026 and suggest strong spin-orbit coupling, probably with phenoxy groups or those of the semiquinone type.

(c) Effect of water on free radicals formation and lignite conversion.

The results of the ESR measurements with water and reactant gases (CO, H$_2$S, H$_2$) are listed in Table 1. In all experiments with H$_2$O, the radical concentrations of ZAP lignite is low considering the very large numbers of radicals known to be formed during pyrolysis ($\approx$ 20.2 x 10^{19} g^{-1}). The determined conversion to volatile products is varied with different pressure of CO. The maximum conversion was achieved mostly in CO = 70 MPa + H$_2$S = 17.5 MPa. This suggests that many of formed radicals were consumed by hydrogen transfer from shift reaction, H$_2$O + CO, shift reaction promoted by H$_2$S throughout COS intermediate compounds and as oil extracted by supercritical water or partly evaporated to reactor were removed during ventilation process. The very narrow linewidth was noted for reactions performed with H$_2$O and reactant gases. Using the relation between ESR spectral linewidth and hydrogen content of coals developed by Retcofsky (29), ΔH_{pp} = 1.6 H - 1.8 where H is weight percent hydrogen, we can conclude that the hydrogen content in the nonvolatile residue is decreased.

SUMMARY

To increase the liquid yields of coal liquefaction, ESR spectra of unconverted coal residues are related to reactor conditions and conversion into volatile products. ESR spectra were obtained for North Dakota Zap lignite treated with various reducing gas atmospheres using a linear-programmed reactor temperature range of 300-500°C. The line shape, spin density, linewidth and g-values were all found to vary with the nature of the reducing gases employed. The spin density of the coal samples increased with increasing concentrations of H_2S in the reactor. Partially superimposed positive and negative signals were recorded when the coal was reacted with H_2S alone. When H_2S is used in conjunction with either H_2 or CO, only two positive signals were observed in the ESR spectra and the spin densities were reduced. The spin density of the reacted coal was minimum when the reaction mixture contained H_2O. The spin density of the samples were inversely related to the percent conversion into volatile products.

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Table 1. ESR Spectral Data and Distillate Conversion Results for ZAP Lignite.[1]

Pressure of gases (MPa)	g value	Linewidth (G)	Spin Density ($\times 10^{19}$)		Conversion (SC) %	Distillate Conversion %
			spins g^{-1} (initial)	spins g^{-1} (final)		
Pyrolysis[2]	2.0011	6.8	20.2 ± 1.9	20.2 ± 1.9	NA	NA
H$_2$ = 34.4	2.0016	6.3	6.1 ± 0.3	10.0 ± 0.5	39.0	NA
CO = 34.4	2.0026	10.6	11.7 ± 0.9	18.7 ± 2.1	37.4	NA
H$_2$, CO = 34.4	2.0026	6.3	4.0 ± 0.5	7.3 ± 0.9	45.2	45.0
H$_2$S = 17.5	2.0035	two signals (+,-)	34.2 ± 3.0	45.0 ± 3.5	24.0	20.0
H$_2$S = 17.5, CO = 34.4	2.0025	6.0	6.3 ± 0.7	10.4 ± 1.2	39.4	39.8
H$_2$S = 17.5; H$_2$,CO = 34.4	2.0012	two signals (+,+)	2.8 ± 1.8	6.2 ± 2.0	54.8	47.8
CO = 34.4; H$_2$O = 0.8 g	2.0017	6.2	3.8 ± 1.2	6.6 ± 1.1	42.4	43.8
CO = 70; H$_2$O = 0.8 g	2.0016	4.4	1.3 ± 0.2	3.2 ± 0.2	59.4	60.9
CO = 70; H$_2$O = 0.8 g; H$_2$S = 17.5	2.0018	2.2	0.5 ± 0.09	2.2 ± 0.4	77.6	78.1
H$_2$S = 17.5; H$_2$, CO = 34.4; H$_2$O = 0.8 g	2.0011	3.9	1.6 ± 0.4	3.8 ± 1.0	57.9	59.9
H$_2$S = 17.5; H$_2$O = 0.8 g	2.0021	two signals (+,-)	19.2 ± 1.9	25.2 ± 3.5	23.8	22.0
S/lignite = 0.94[2,3]	2.0036	6.25	11.9	11.9	NA	NA
S/lignite = 0.33[2,3]	2.0036	two signals (+,-)	24.7	24.7	NA	NA

[1]Experimental conditions for liquefaction, water = 0.8 g, pressure of gases are listed in the Table, reaction temperature, 300-500°C, reaction time 1 hr, ventilation at 500°C.
[2]Reactions have been performed in sealed capillary tubes with no charged gases.
[3]Weight ratio of sulfur to lignite.

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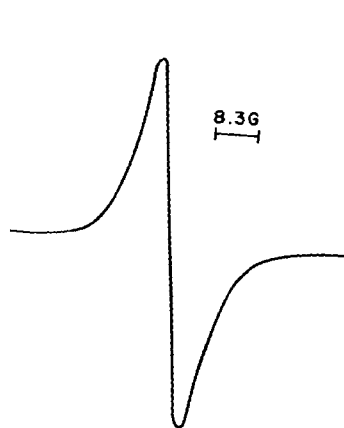
Figure 1. ESR spectrum of ZAP lignite.
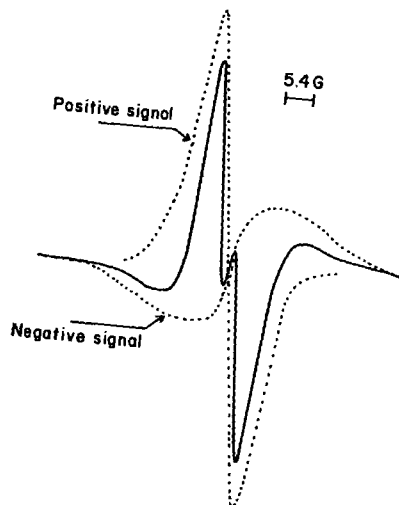
Figure 2. ESR spectrum of ZAP lignite after reaction with H_2S.
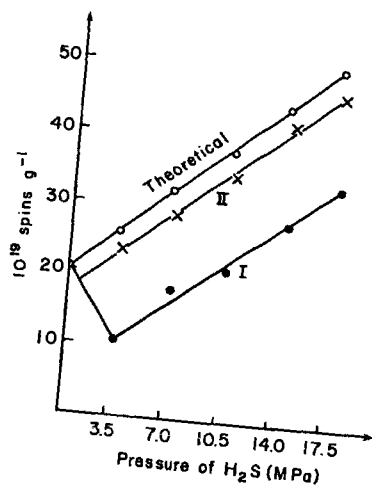
Figure 3. Variation of total radical concentration with pressure of H_2S.
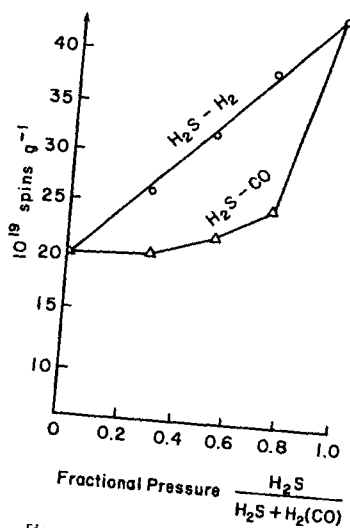
Figure 4. ESR g-value of ZAP lignite after reaction with H_2S at linear programmed temperature, 300-500°C.

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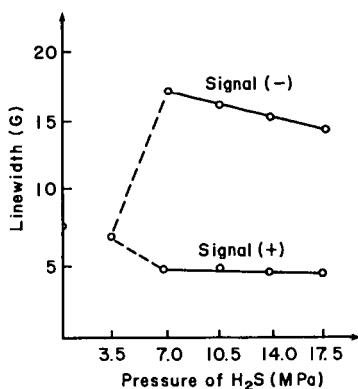
Figure 5. Variation of ESR spectral linewidth for recorded positive (+) and negative (-) signals with pressure of H_2S.
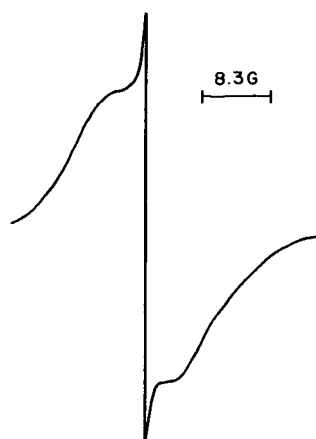
Figure 6. ESR spectrum of ZAP lignite after reaction with H_2S-H_2 at linear programmed temperature, 300-500°C.
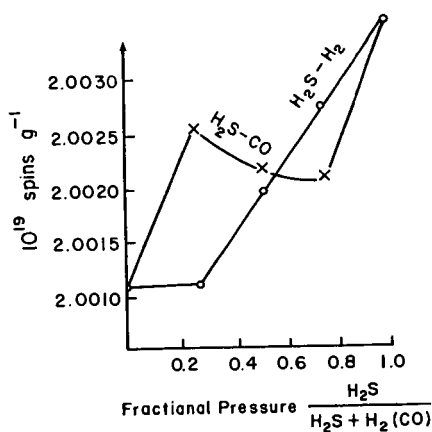
Figure 7. Variation of spin concentration with fractional pressure of H_2S.
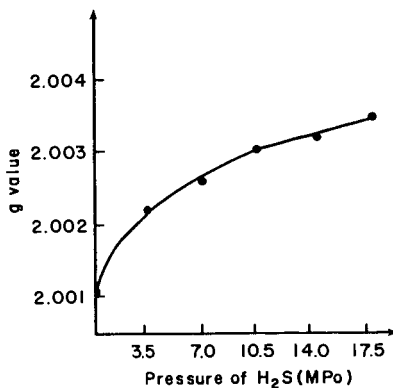
Figure 8. ESR g value of ZAP lignite versus fractional pressure of H_2S.

STRUCTURAL FEATURES OF PRODUCTS DERIVED FROM WATER-ASSISTED
LIQUEFACTION OF BITUMINOUS COALS

John A. Ruether, Richard G. Lett, and Joseph A. Mima

Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

INTRODUCTION

In recent years, several research teams interested in obtaining liquid fuels from coal have investigated approaches that involve adding substantial amounts of water with the coal during processing. Although the approaches taken by the different groups vary considerably, all groups cite the low cost of water -- as a reactant, extractant, or transport medium -- to be a potential advantage for aqueous liquefaction compared to more conventional processes. For some processes, the vapor pressure of water at reaction temperature makes a very considerable contribution to the total pressure required in the reaction section. Further research will show if the necessity of high pressure in aqueous systems can be avoided or if advantages in terms of product quality and yields realized through use of water will compensate for higher pressure requirements.

Work at our laboratory has investigated the interplay of organic solvent, water, and water-soluble catalysts on conversion of coal to soluble products in the presence of hydrogen gas [1,2,3]. At constant hydrogen partial pressure and temperature, conversion increases both with an increase in water density and an increase in water-to-coal ratio in the reactor. The mechanism by which water aids conversion is not known, but some experiments with deuterium oxide indicated that hydrogen-oxygen bonds in water were not being broken. In the presence of water, especially when a water-soluble molybdenum catalyst is also present, the full benefit of having an organic solvent present is achieved at solvent-to-coal ratios as low as 0.25. In addition, organic solvent, water, and catalyst are complementary in promoting conversion, and high conversions can be obtained by various combinations of these three aids to hydroliquefaction reactions.

These findings have led us to continue to conduct reactions with various combinations of coal-to-solvent and coal-to-water ratios, of temperature, and of hydrogen partial pressure. Our aim is to identify advantageous reaction conditions that may be used in a continuous process that employs a lower solvent-to-coal ratio for the feed stream than is used in current donor solvent processes. This work examines the structural features of coal liquids produced under a variety of unconventional reaction con-

ditions. Some questions of interest are the following: For reaction at low solvent-to-coal ratios and high water partial pressure, do liquid products resemble those from conventional donor solvent processes, or take on some characteristics of pyrolysis products? Is there evidence of incorporation of oxygen from water in the products? What is the effect of reaction temperature on product characteristics? To examine these questions, reactions were carried out with two Illinois No. 6 bituminous coals, and the liquid products were extensively analyzed.

EXPERIMENTAL

Hydroliquefaction Reactions

Batchwise liquefactions of two Illinois No. 6 bituminous coals were carried out using varying values of organic vehicle-to-coal and water-to-coal in the charge. All reactions were carried out with use of a water-soluble catalyst, ammonium heptamolybdate, in the concentration range 0.08-0.27 wt% molybdenum on dry coal. Gaseous hydrogen was employed in all runs. Ultimate analyses of the two coals, Burning Star and River King, are shown in Table 1. Two different hydrogen-donor solvents were also employed in this work. A composite Lummus solvent was derived from the 2SCT series of experiments (LCF-9 runs) with Burning Star coal on the Lummus Integrated Two-Stage Liquefaction (ITSL) Process Development Unit. A second solvent, designated HWSRC, was resid from the hydrotreater at the Wilsonville Advanced Coal Liquefaction Facility, produced during Run 242 with Burning Star coal.

Table 1. Elemental and Ash Analyses (wt%) of Illinois No. 6 Coals.

	Burning Star		River King	
	mf	maf	mf	maf
H	4.74	5.47	4.65	5.27
C	67.5	77.9	65.2	73.9
O	--	$(12.1)_{diff.}$	--	$(15.5)_{diff.}$
N	0.8_8	1.0	0.9_6	1.1
S	3.0	3.5	3.7	4.2
Ash	10.6	--	13.8	--

Reactions were carried out in a stirred one-liter autoclave. Reaction conditions employed are shown in Table 2. Coal, organic solvent, water, and catalyst were charged batchwise. Hydrogen was charged cold to the reactor at the desired total reaction pressure. As the reactor temperature rose during the heat-up period, hydrogen gas was vented via a back pressure control valve to maintain the total pressure. During the course of the

reaction, the partial pressure of hydrogen decreased and that of other components increased. The total pressure and the hydrogen partial pressure at reaction temperature at the end of each run are shown in Table 2. In one run (H-14), the reaction was carried out under 1900 psig partial pressure of nitrogen. Reaction times were 30 or 60 minutes and were measured from the time the desired operating temperature was established. Following a reaction, the reactor was cooled overnight to room temperature. Product gases were vented to a gas holder, then metered and sampled. Light oils (n.b.p. $\leq$293°C) and water were stripped from the reactor by vacuum distillation. The remaining heavy liquids and solids were dissolved in toluene and removed from the reactor. The toluene was stripped from the heavy products that were subsequently analyzed for THF-, benzene-, and cyclohexane-insolubles to determine conversions and product distributions. Asphaltenes are defined as material soluble in benzene and insoluble in cyclohexane. Heavy oils are material soluble in cyclohexane.

Chemical and Instrumental Analyses

The vacuum-stripped products were separated into methylene chloride solubles and insolubles to facilitate further analyses. Elemental analyses were performed on both the methylene chloride soluble and insoluble portions. Molecular weight determinations were performed on methylene chloride solubles by vapor pressure osmometry. Quantitative measurements of phenolic O-H, and relative concentrations of N-H in the methylene chloride soluble fractions were made by near-infrared procedures. High resolution ^{1}H and ^{13}C NMR spectra of the methylene chloride soluble fractions were acquired on a Varian XL-100 spectrometer.

RESULTS

Solvent Analysis

Conversions to THF and benzene solubles, and yields of hydrocarbon products are shown in Table 3. Although all reaction conditions were not varied systematically, some general observations can be made. High THF conversions (greater than 90%) and high benzene conversions (approaching 90%) were achieved with both of the coal and solvent combinations tested, River King/Lummus and Burning Star/HWSRC. Use of low hydrogen pressure results in low THF conversions (Runs H-14 and H-17). With a low temperature, high THF conversions may be obtained, but benzene conversions are reduced (Runs H-12 and H-16). In systems with solvent present, high conversions are obtained both with and without added water, but at lower pressure when water is absent (Runs H-10, H-24, and H-30).

Elemental Analyses of Feed and Product Fractions

Table 1 shows that analyses of the two coals are very similar, as expected. Tables 4 and 5 give the elemental analyses and average molecular weight of the methylene chloride soluble and insoluble fractions, respectively, of the two solvents used -- composite Lummus ITSL solvent and hydrogenated Wilsonville thermal resid (HWSRC). Essentially all the HWSRC is soluble in methylene chloride. The tables disclose several significant

Table 2. Experimental Reaction Conditions Associated with Liquefaction Products Analyzed

Autoclave Run No.	Added Solvent	Solvent/Coal	Water/Coal	Catalyst wt% Mo on Coal	Temp. (°C)	Time (min.)	Final Pressure, psig P_Total	P_{H_2}
H-10	Lummus	0.33	0.25	0.14	427	60	4250	1750
H-12	None	0	0.44	0.10	370	30	4050	1760
H-14	Lummus	0.33	0	0.27	427	60	4510 (3160 N_2)	520
H-16	Lummus	0.33	0.25	0.08	370	60	4690	2820
H-17	None	0	0.44	0.10	427	60	3880	720
H-24	HWSRC	0.33	0	0.10	427	60	2170	1530
H-30	HWSRC	0.33	0	0.10	427	60	1730	1180

All runs with Illinois No. 6 coal -- River King (H-10 through H-16) and Burning Star (H-17 through H-30).

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Table 3. Conversion to Solubles and Yields in Liquefaction Experiments

Autoclave Run No.	Conversion (wt%, maf Coal)		Net Yield (wt%, maf Coal)			
	THF	Benzene	Asphaltenes	Heavy Oils	Light Oils	Hydrocarbon Gases
H-10	90.2	87.6	17.7	66.7	9.0	8.7
H-12	89.7	55.0	29.7	17.9	1.0	---
H-14	71.9	59.8	16.7	43.8	9.0	7.1
H-16	92.7	66.2	42.1	37.7	3.0	---
H-17	84.1	----	38.0	11.8	3.8	5.3
H-24	91.4	86.6	27.2	68.0	8.6	6.3
H-30	90.8	83.9	28.6	59.7	10.6	5.5

Table 4. Elemental Analyses and Number Average Molecular Weights of Methylene Chloride Soluble Fractions of Solvents and Heavy Aqueous Liquefaction Products.

Sample	C	H	O	N	S	H/C	$\bar{M}_n$[a]
Composite Lummus ITSL Solvent	90.4	6.9_3	1.5	0.7_0	0.4_5	0.91_3	345
HWSRC Solvent	89.6	7.4_6	1.9	0.8_3	0.2_7	0.99_0	587
H-10	88.5	7.4_6	2.6	1.1	0.3_5	1.0_0	315
H-12	84.1	7.2_7	6.0	1.1	1.5_7	1.0_3	573
H-14[b]	89.4	6.6_3	2.3	1.2	0.5_0	0.88_8	318
H-16	86.4	7.2_8	4.2	1.1	1.0_3	1.0_0	408
H-17	87.8	7.1_0	3.2	1.4	0.5_2	0.96_4	340
H-24	88.8	7.4_7	2.4	1.1	0.3_1	1.0_0	343
H-30	89.0	7.0_3	2.3	1.3	0.3_5	0.94_1	362

[a] VPO in pyridine @ 80°C.

[b] Average of two determinations.

Table 5. Elemental Analyses (C,H,N) of Methylene Chloride Insoluble
Fractions of Solvents and Heavy Aqueous Liquefaction Products
on an Ash-Free Basis.

Sample	C	H	N	H/C
Composite Lummus ITSL Solvent	86.4	4.9_4	2.1	0.68_2
H-10	74.8	4.5_2	2.4	0.72_0
H-12	81.3	5.7_6	1.5	0.84_4
H-14	85.4	4.2_4	1.6	0.59_1
H-16	80.8	5.8_3	1.6	0.85_9
H-17	89.6	4.9_8	1.9	0.66_2
H-24	87.7	5.1_7	2.1	0.70_2
H-30	88.1	5.0_0	2.2	0.68_1

differences between the solvents. The Lummus solvent is of lower molecular
weight and is less hydrogenated. The average molecular weight of the HWSRC
is in the range expected for soluble nondistillate coal-derived resids.

Tables 4 and 5 also contain elemental analyses for the methylene
chloride soluble and insoluble fractions, respectively, of the residual
reaction products after the light oil has been stripped off. The hydrogen
content of the methylene chloride soluble fractions of the products is ~7%,
similar to that of the added hydrogen donor solvents. Although the relative
yields of methylene chloride solubles are considerably reduced in the runs
made at 370°C vs. 427°C, the H/C ratio of the solubles does not appear to
be highly temperature dependent. All of the methylene chloride solubles are
higher in oxygen than the added hydrogen donor solvents (which have been
catalytically hydrotreated). The oxygen content of the products from the
runs at 370°C is considerably higher than that of the runs at 427°C. How-
ever, excluding the 30-minute Run H-12 with added solvent in which poor con-
version to methylene chloride solubles was achieved, the oxygen determi-
nations in Table 4 are in the range expected for conventional direct lique-
faction products of similar average molecular weight derived from Illinois
No. 6 coal.

Heteroatomic Functionality

Infrared analyses of the O-H and N-H functionality in the solvents and heavy
products are summarized in Table 6. The fraction of oxygen present as
phenolic OH in the methylene chloride solubles appears to be between 0.3 and
0.4, and follows the total oxygen in Table 4 as determined by elemental
analysis. The results reflect the fact that hydrogenolysis of carbon-oxygen
bonds is less extensive at 370°C than at 427°C. Also, the methylene

Table 6. Dilute Solution Infrared Analyses of Methylene Chloride
Soluble Solvent Fractions and Product Fractions

	%O as Free OH	Fraction of Total O as Free OH	Est.% N as N-H	Fraction of Total N as N-H
Solvent				
Composite Lummus ITSL	0.4_7	0.3_2	0.2_5	0.3_6
HWSRC	0.4_4	0.2_3	0.2_8	0.3_4
Autoclave Run No.				
H-10	0.9_7	0.3_7	0.3_2	0.3_0
H-12	1.7	0.2_9	0.2_0	0.1_9
H-14	0.8_8	0.3_5	0.4_4	0.4_0
H-16	1.3	0.3_2	0.2_7	0.2_5
H-17	1.5	0.4_7	0.4_8	0.3_5
H-24	0.9_9	0.4_1	0.4_3	0.4_0
H-30	0.9_4	0.4_1	0.4_4	0.3_4

chloride solubles from runs made without added hydrogen donor solvent tend
to be higher in phenolic O-H and oxygen than from runs made with added
solvents that are relatively depleted in oxygen. The estimated fraction of
the nitrogen present as pyrrolic N-H is from 0.3 to 0.4, values that are
consistent with similar infrared analyses of other direct liquefaction
products derived from Illinois No. 6 (Burning Star) coal.

Average Structural Parameters

As a means of further comparing the heavy dewatered products, average
structural parameters associated with the methylene chloride soluble solvent
and product fractions have been calculated. These parameters should not be
viewed as a means of constructing fictitious "average structures" for these
very complex fractions but as a means of condensing a large body of diverse
information into a set of correlative parameters that may prove useful for
comparing samples and drawing general conclusions.

The mean structural parameters tabulated in Table 7 have been calcu-
lated by the Brown and Ladner procedure[*] from elemental analysis, ^{1}H NMR,
and NIR data. The aliphatic H/C ratio was assumed to be two for all groups
having proton resonances in the H_α and H_β regions, and three for groups

Table 7a. Mean Structural (Brown and Ladner) Parameters of Methylene
Chloride Soluble Fractions of Hydrogen Donor Solvents

| | Solvent | |
	Composite Lummus ITSL	HWSRC
Carbon Aromaticity, f_a	0.73	0.62
Hydrogen Aromaticity, H_{ar}^*	0.37	0.20
Degree of Aromatic Ring Substitution, σ	0.30	0.49
H/C Ratio of Unsubstituted Aromatic Units, H_{aru}/C_{ar}	0.64	0.61
Average Alkyl Substituent Chain Length, n	2.2	2.2

(mostly methyl) having resonances in the H_γ region. This "prescription" generally yields calculated aromaticity values for bituminous coal lique- faction products that agree with the direct ^{13}C NMR measurements.

The mean structural parameters of the added donor solvents are given in Table 7a. The calculated aromaticities reflect the relative hydrogen con- tent of the solvents as determined by elemental analysis (Table 4). The degree of aromatic ring substitution (σ), which is an estimate of the frac- tion of aromatic ring edge atoms bearing a substituent, is higher for more hydrogenated HWSRC. In part, this is a consequence of the fact that the Brown and Ladner approach treats hydroaromatic rings as two alkyl substi- tuents with an average carbon chain length of two. In both solvents, the estimated average alkyl substituent chain length is about two, i.e., in common with most heavy coal liquefaction products, the most prominent alkyl substituents are methyl groups and hydroaromatic rings as opposed to long chain alkyl groups. The calculated H/C ratio of the unsubstituted aromatic units (H_{aru}/C_{ar}) imply that the average aromatic units in both solvent fractions are larger than three rings and that the average size of such units is larger in the HWSRC than in the methylene chloride soluble fraction of the composite Lummus ITSL solvent. However, it should be realized that this parameter is an insensitive indicator of the exact ring cluster size for systems containing more than three aromatic rings. In addition, since the Brown and Ladner treatment does not acknowledge the presence of hetero- cyclic rings, care should be exercised in attaching more than qualitative significance to these results.

None of the structural parameters characterizing the methylene chloride soluble fractions of the heavy dewatered aqueous liquefaction products (Table 7b) are significantly different from those of direct liquefaction products of similar hydrogen content and molecular weight range derived from Illinois No. 6 coal. As an example, analyses of two light thermal resids

Table 7b. Mean Structural (Brown and Ladner) Parameters of Methylene
Chloride Soluble Product Fractions Calculated Using ^{1}H-NMR Data

	Autoclave Run No.						
	H-10	H-12	H-14	H-16	H-17	H-24	H-30
Carbon Aromaticity, f_a	0.68	0.62	0.76	0.66	0.69	0.67	0.70
Hydrogen Aromaticity, H_{ar}^*	0.34	0.22	0.45	0.27	0.33	0.30	0.33
Degree of Aromatic Ring Substitution, σ	0.33	0.48	0.27	0.39	0.33	0.37	0.36
H/C Ratio of Unsubstituted Aromatic Units, H_{aru}/C_{ar}	0.76	0.70	0.72	0.68	0.68	0.71	0.69
Average Alkyl Substituent Chain Length, n	1.9	2.0	1.7	2.1	2.2	2.0	1.9

(LTR's) from Non-Integrated Two-Stage Liquefaction (NTSL) experimentation at
Wilsonville are summarized in Table 8. In Run 236 the dissolver was
operated under "mild" severity NTSL conditions (419°C, 2000 psig H_2,
30 lb/hr ft^3 coal space rate), while in Run 241 the dissolver was operated
under "moderate" severity NTSL conditions (430°C, 2400 psig H_2, 20 lb/hr ft^3
coal space rate). The aqueous liquefaction fractions tend to be only
slightly lower in average molecular weight and slightly more hydrogenated
than the light thermal resid from NTSL Run 236. After allowing for the
diluting effect of the added donor solvent, the percent oxygen appears to be
slightly lower in the aqueous liquefaction product fractions than in the
LTR's, but the fraction of oxygen as OH is similar in both cases. Likewise,
the estimated wt% nitrogen as pyrrolic N-H and fraction of the total
nitrogen as N-H are similar for both types of products.

Table 8a. Elemental Analyses and Number Average Molecular Weights of
Methylene Chloride Soluble Fractions of Light Thermal Resids
from Liquefaction of Illinois No. 6 (Burning Star) Coal at
the Wilsonville ACLTF.

	Elemental Analysis (wt%)						
Run No.	C	H	O	N	S	H/C	$\bar{M}n$
236	85.1	6.7$_0$	5.5	1.6	1.1	0.938	464
241	88.1	6.1$_9$	3.3	1.6	0.8	0.836	453

Table 8b. Near-Infrared Analyses of Methylene Chloride Soluble
Fractions of Light Thermal Resids.

Run No.	% O as Free OH	Fraction O as Free OH	Estimated %N as NH	Fraction N as NH
236	1.8_6	0.3_7	0.4_4	0.3
241	1.4_2	0.4_6	0.5_1	0.3

Table 8c. Mean Structural (Brown and Ladner) Parameters of Methylene
Chloride Soluble Fractions of Light Thermal Resids.

	Light Thermal Resid	
	Run 236	Run 241
Carbon Aromaticity, f_a	0.70	0.75
Hydrogen Aromaticity, H_{ar}^*	0.32	0.35
Degree of Aromatic Ring Substitution, σ	0.38	0.36
H/C Ratio of Unsubstituted Aromatic Units, H_{aru}/C_{ar}	0.69	0.61
Average Alkyl Substituent Chain Length, n	1.8	1.7

DISCUSSION

From the viewpoint of general structural features such as aromaticity, hydrogen distribution, and heteroatom functionality, the methylene chloride solubles of the vacuum-stripped products from aqueous liquefaction of Illinois No. 6 coal in the presence of added Mo catalyst are remarkably similar to conventional direct liquefaction products of the same molecular weight range derived from this coal. They do not exhibit features characteristic of coal pyrolysis products, such as a predominance of highly condensed polycyclic aromatic structures with a low degree of ring substitution and low phenolic content. These results are consistent with recent reports of the product composition from dissociation of Illinois No. 6 coal in base-catalyzed CO and H_2O systems.[5] In the latter experiments, no dramatic differences in composition of the toluene soluble product fractions were found over a wide range of conversion. Also, chromatographic profiles of the toluene solubles from liquefaction of Illinois No. 6 coal in CO and H_2 and in tetralin were similar, although the mechanism of coal dissociation in the two systems must be quite different. A distinction has been made

between thermal severity (temperature, residence time) and reduction severity (specific reactivity of the reducing species). The inference has been made that similar weak bonds in the coal macromolecular structure are being broken in both aqueous and conventional coal liquefaction systems and that the products reflect some statistical regularity or uniformity in the distribution of chemical entities that constitute the coal macromolecular structure. Thus, although increasing the reduction (chemical) severity may increase the rate of bond breaking by chemical rather than thermal mechanisms, the observed result is primarily a larger number of liberated fragments rather than a change in their character. The present work indicates a similar interpretation is consistent with the reaction systems studied here.

In the present experiments, temperature is the most obvious variable influencing both yields and product composition. There appears to be the same trade-off in the aqueous liquefaction of catalyst-impregnated coal as in conventional thermal liquefaction using hydrogen donor solvents without added catalyst. Lower reaction temperatures (<400°C) tend to favor hydrogenation over cracking and result in reduced hydrocarbon gas production, lower distillate yields, and higher yields of heteroatom-rich resid that may be soluble in polar solvents. Higher reaction temperatures (>400°C) favor thermolysis and hydrogenolysis over hydrogenation. A higher yield of distillate may result, but the remaining resid tends to become more refractory in nature, and the production of light hydrocarbon gases increases.

The chemical role of the water, if any, in the catalyst-impregnated coal and aqueous liquefaction system is not clear from the elemental and structural analyses of the products. Use of water as a vehicle with added ITSL solvent and catalyst appears to have given no better results than hydrogenation of the catalyst-impregnated coal in the presence of small quantities of a heavier, slightly more hydrogenated solvent at moderate pressures. There is no evidence for any significant net incorporation of oxygen; the water-assisted liquefaction products are not any higher in total oxygen or phenolic OH than conventional thermal-stage coal dissociation products of Illinois No. 6 coal.

In terms of H/C ratio, and carbon and hydrogen aromaticities, the methylene chloride soluble fractions of the residual liquefaction products exhibit characteristics typical of donor solvent liquefaction products. As seen in Table 7, except for Run H-14, the aromaticities of the reaction products were less than that of the Lummus ITSL solvent and comparable to that of the HWSRC. Table 8c discloses that the carbon and hydrogen aromaticities of light thermal resids produced at Wilsonville in NTSL Runs 236 and 241 are higher on average than those for the reaction products of this work. The analytical data indicate that the latter products have properties typical of similar molecular weight products that were produced in conventional donor solvent processes.

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LIQUEFACTION CO-PROCESSING OF COAL AND SHALE OIL AT LOW SEVERITY CONDITIONS

R. L. Miller and R. M. Baldwin
Chemical Engineering and Petroleum Refining Department
Colorado School of Mines
Golden, Colorado 80401

ABSTRACT

Results are reported for a series of single stage batch reactor exper-
iments in which Wyodak subbituminous coal and shale oil derived from
medium grade Colorado oil shale were co-processed at low severity
reaction conditions using CO/H_2O as reducing agent. Distillate yields
of over 85 wt% MAF coal with hydrogen equivalent consumptions of about
1.0 wt% MAF coal were obtained at 600°F reaction temperature. Results
from blank shale oil runs at the same mild reaction conditions
suggested that shale oil residuum reactivity was enhanced in the
presence of coal or primary coal-derived products.

INTRODUCTION

The possibility of liquefying coal at low severity reaction conditions
($\leq$700°F) has intrigued researchers for many years. As early as 1921,
Fischer and Schrader (1) reported production of an ether-soluble
material from coal at 660°F using carbon monoxide and water as re-
ducing agent. More recently other groups including the Pittsburgh
Energy Technology Center (PETC) (2), the North Dakota Energy Research
Center (3-4), SRI (5-7), and Carbon Resources, Inc. (8) have inves-
tigated various methods of utilizing H_2, CO/H_2O or $CO/H_2/H_2O$ (syngas)
in low severity liquefaction processes. Many incentives exist for
converting coal at milder reaction conditions. The most important of
these are listed below:

1) Reduced H_2 (or CO) consumption and hydrocarbon gas make

2) Better distillate and residuum product quality, since car-
   bonization and other retrogressive reactions are suppressed to
   a large extent

3) Production of less refractory residuum which is more sus-
   ceptible to hydrocracking in a conventional second stage
   hydrotreater or hydrocracker

4) Significant energy savings associated with lower operating
   temperatures

5) Less severe slurry handling and materials of construction
   problems

A number of studies have been reported in which coal and non-
coal-derived heavy oil have been co-processed at severe reaction
conditions to obtain valuable distillable liquid products (9-11). In
some cases, larger distillate yields were obtained by co-processing
coal and heavy oil than by processing each feed separately. Shale oil
has been identified as a particularly promising feed, due in part to
the high heterocyclic basic nitrogen content of the oil (12). In
spite of the advantages of operating at milder conditions, little work
on low severity co-processing has been reported.

The objective of this paper is to report yield and conversion data from a series of single-stage low severity co-processing runs using Wyodak subbituminous coal and shale oil derived from medium grade Colorado shale. Blank shale oil runs (no coal added) were also completed at low severity conditions to estimate the individual distillate yield contributions of coal and shale oil.

EXPERIMENTAL PROCEDURE

Wyodak subbituminous coal sample Wyo-3 was used as feed coal in the low severity liquefaction co-processing experiments. The ultimate analysis for this sample is presented in Table I. Sampling and preparation details of the coal have been reported elsewhere (13,14). Previous reactivity studies performed on four Wyodak subbituminous coals including Wyo-3 indicated that Wyo-3 was an extremely reactive coal at representative direct liquefaction reaction conditions (13,15). The high degree of reactivity was primarily attributed to the high organic sulfur and reactive maceral (vitrinite and exinite) content of Wyo-3 coal. Coal samples were dried to less than 1.0 wt% moisture content before use.

Two shale oil samples were used in low severity liquefaction co-processing runs. Solvent A-5 was a full boiling range sample of shale oil obtained from the Western Research Institute (formerly the Laramie Energy Technology Center of the Department of Energy). This sample was produced from thermal retorting of medium grade (29 gal/ton) Colorado oil shale. Solvent A-6 was prepared by mildly hydrotreating a portion of sample A-5 in a two liter batch Autoclave Magnedrive II reactor at 650°F for one hour with an initial cold hydrogen pressure of 2000 psig. Nalcomo 477 cobalt molybdate catalyst was used to hydrotreat the shale oil. Catalyst samples were thermactivated at 1000°F for two hours in a muffle furnace prior to use. Approximately 0.6 wt% hydrogen was consumed by the shale oil during hydrotreating. Properties of shale oil samples A-5 and A-6 are presented in Table II. Approximately 50 wt% of the nitrogen in these samples existed in quinoline-type or hydroquinoline-type molecular structures.

Runs were carried out in a 60 cm^3 stirred microautoclave reactor system designed and constructed at the University of Wyoming. This reactor was similar to larger Autoclave batch reactors except that heating was accomplished with an external high temperature furnace. At the end of each run, the reactor and its contents were quenched with an icewater batch. This reactor system provided the benefits of small tubing bomb reactors [quick heatup (~1 min. from room temperature to 650°F) and cooldown (~30 sec. back to room temperature)], while at the same time insuring sufficient mechanical agitation of the reactants with an Autoclave Magnedrive II stirring assembly to minimize hydrogen mass transfer effects. The system was also designed so that the reactor pressure was very nearly constant throughout an experiment. Two iron-constantan thermocouples attached to a Fluke 2175A digital thermometer were used for temperature measurements. One thermocouple measured the temperature of the reactor contents, while the other measured the temperature of the reactor wall. Reactor pressure was monitored using a 0 - 5000 psi Marsh pressure gauge.

In these runs, carbon monoxide and water were used as reducing agent, with hydrogen being produced via the aqueous phase water-gas shift reaction. Reaction conditions were studied in the range: 600-650°F

reaction temperature, 1000-1500 psig initial cold carbon monoxide pressure, and 15-60 minutes reaction time. Distilled water is an amount equal to 50 wt% of the dry feed coal was charged to each reactor run. Iron sulfate (5 wt% dry feed coal) was used as a disposable catalyst.

Gaseous products were analyzed using gas chromatography. Water and distillate yields were measured by distilling portions of the combined liquid-solid product mixture to an 850°F endpoint in a micro-distillation apparatus. Additional portions of the liquid-solid product mixture were extracted in a Soxhlet extraction apparatus using cyclohexane, toluene, and pyridine. Details of the experimental procedures used in this work have been reported (9).

RESULTS AND DISCUSSION

Using data collected with the analytical procedures described, detailed yield and conversion results were computed for each lique-faction co-processing run. Details of the computational methods used in this study have been described previously (9). For purposes of the present discussion, process performance will be monitored using the following two parameters: C_4-850°F distillate yield (wt% MAF coal basis), and pyridine conversion (wt% MAF basis). Pyridine conversion is defined as a measure of the extent of conversion of all feeds (coal and non-coal-derived heavy oil) to pyridine soluble products. How-ever, since both A-5 and A-6 shale oil samples were completely soluble in pyridine and negligible coking of the shale oil occurred at low severity reaction conditions, pyridine conversion values reported in this paper are direct measures of the extent of coal conversion in the co-processing runs.

Effect of Shale Oil Prehydrotreatment

Figure 1 shows distillate yield results from co-processing runs completed using Wyo-3 coal and either A-5 or A-6 shale oil at 600°F and 1500 psig initial cold CO pressure. This data clearly shows that mild hydrotreatment of the shale oil greatly enhances co-processing performance. Coal conversion also increased significantly when A-6 shale oil was used in place of A-5 shale oil. Distillate yields of over 85 wt% MAF coal (58 wt% MAF coal and 850°F+ shale oil) and pyri-dine soluble coal conversions of nearly 60 wt% MAF basis were obtained with A-6. Previous high severity co-processing studies using Wyo-3 and A-6 also demonstrated the beneficial effect of prehydrotreatment. The enhancement at low severity conditions can be attributed to: 1) increased hydrogen donor ability of the hydrotreated shale oils and 2) increased concentration of partially hydrogenated basic nitrogen compounds such as tetrahydroquinoline and piperidinopyridine in the shale oil. These compounds are known to promote coal dissolution and catalyze the aqueous phase water-gas shift reaction.

Effect of Reaction Temperature

Figures 2 and 3 present yield and conversion results for co-processing runs completed with Wyo-3 and A-6 at 600°F and 650°F. These data show that process performance improved at lower reaction temperature. This effect can be at least partially attributed to the favorable thermo-dynamic equilibrium of the water-gas shift reaction at lower temper-atures.

Effect of Initial Carbon Monoxide Pressure

The effect of varying the initial CO pressure is illustrated in Figure 4. At 600°F reaction temperature, increasing the CO pressure from 1000 to 1500 psig more than doubled the distillate yield over the entire range of reaction times studied. These data indicate that relatively high pressure is required to achieve sufficient CO solubility in the aqueous phase for the water-gas shift reaction to proceed at a satisfactory rate.

Results from Blank A-6 Shale Oil Runs

In an attempt to estimate the amounts of distillate derived from coal and from shale oil, several blank shale oil runs (no coal added) were completed. Results from both high severity and low severity blank runs are shown in Figure 5. These data were then used to estimate the amount of distillate attributable to the shale oil feed in each co-processing run. Estimates of the coal-derived distillate production were computed by assuming that half of the total coal-derived cyclohexane soluble product was distillate. Results of these calculations are shown in Figure 6. Both low severity and high severity runs are included in this figure for comparison purposes. In each co-processing run, additional distillate in excess of that predicted by the blank shale oil runs was obtained. Thus, it appears likely that the reactivity of shale oil residuum towards distillate production is enhanced in the presence of coal or primary coal-derived products.

CONCLUSIONS

A series of low severity liquefaction co-processing runs has been completed using Wyodak subbituminous coal and two shale oil samples. Results indicated that prehydrotreatment of the shale oil, lower reaction temperature, and higher initial CO pressure all contributed to enhanced process performance. Distillate yields in excess of 85 wt% MAF coal were obtained at 600°F, 1500 psig CO pressure, and 60 minute reaction time. Results from blank shale oil experiments suggested that overall distillate yield could be maximized by co-processing coal and shale oil rather than processing the two feeds separately.

ACKNOWLEDGEMENTS

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Table I

Ultimate Analysis of Wyodak
Subbituminous Coal Wyo-3

Ultimate Analysis, wt% dry basis

Carbon	58.2
Hydrogen	4.3
Nitrogen	0.8
Sulfur	2.9
Sulfate	0.8
Pyrite	0.9
Organic	1.2
Oxygen (difference)	13.9
Ash	19.9

Table II
Properties of Shale Oil Samples

Sample	A-5	A-6
Wt% Distilled		
Water	0.7	0.1
350°F	4.2	10.3
350°F-500°F	9.6	18.3
500°F-650°F	18.8	22.5
650°F-850°F	39.0	29.8
850°F+	27.7	19.0
Ultimate Analysis, wt% dry basis		
Carbon	83.3	84.7
Hydrogen	12.1	12.9
Nitrogen	1.4	1.2
Sulfur	0.5	0.4
Oxygen (difference)	2.7	0.8
Ash	0.0	0.0

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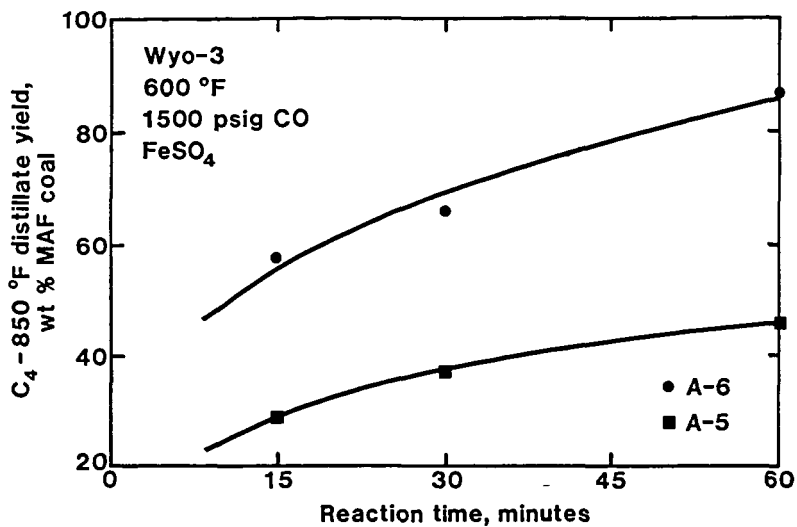
Figure 1. Distillate Yield as a Function of Reaction
Time and Shale Oil Feed
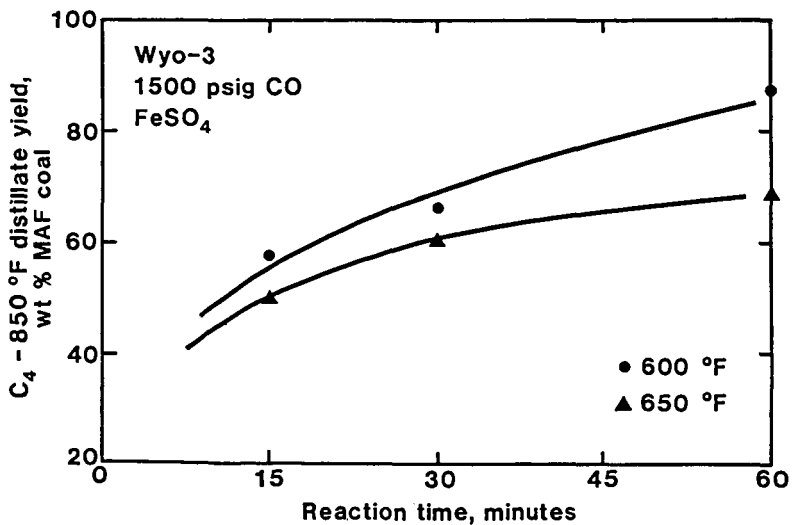
Figure 2. Distillate Yield as a Function of Reaction
Time and Temperature
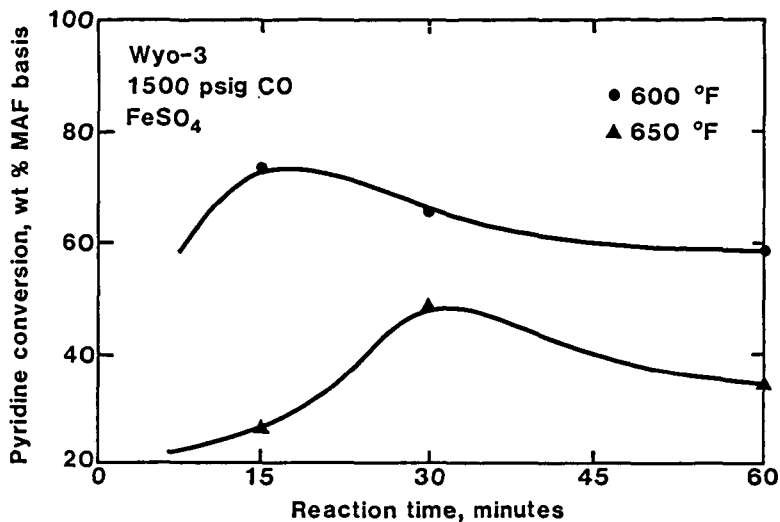
Figure 3. Pyridine Conversion as a Function of Reaction Time and Temperature
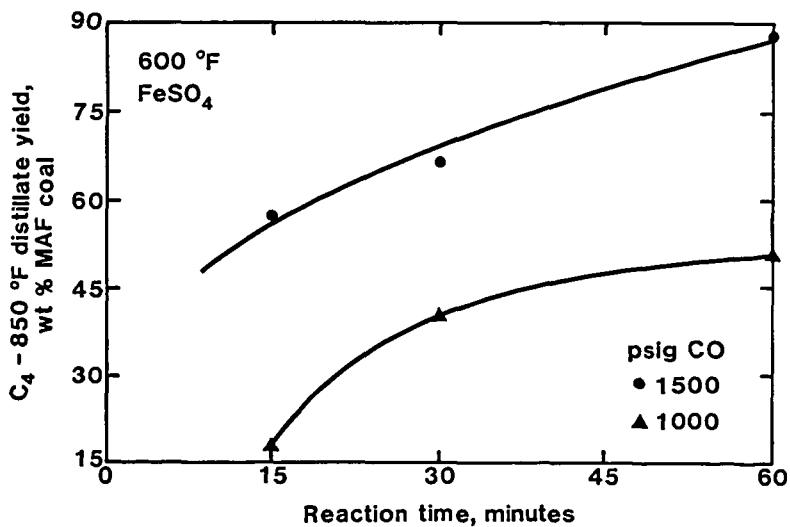

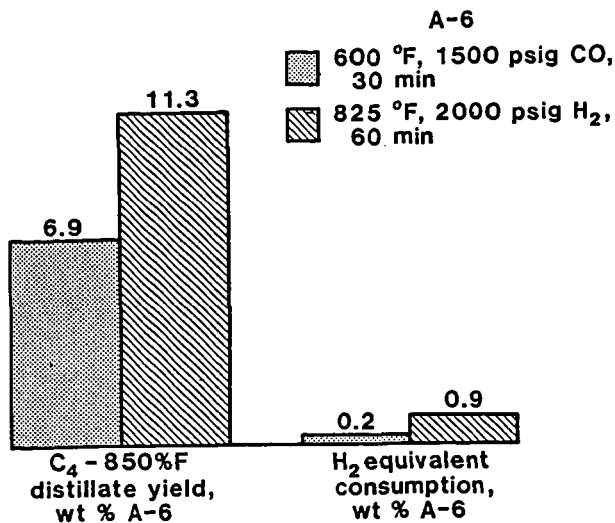Figure 4. Distillate Yield as a Function of Reaction Time and CO Pressure

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Figure 5. Results from Blank Shale Oil Runs at Low
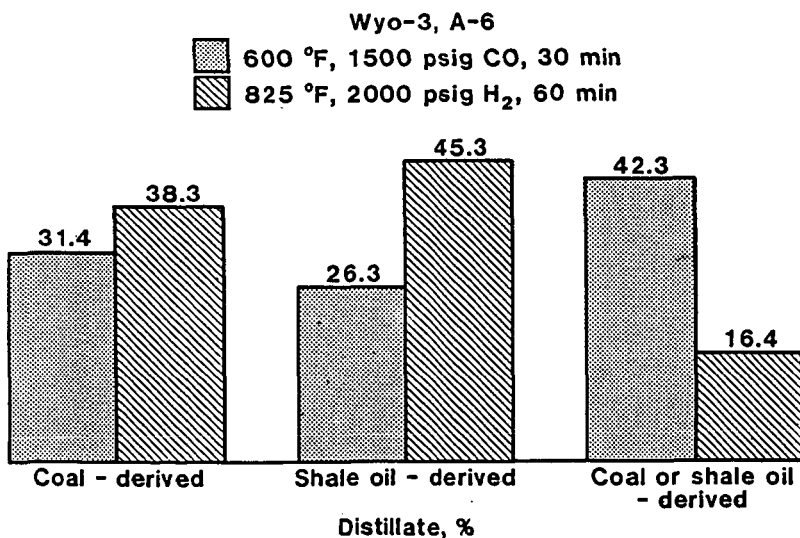and High Severity Reaction Conditions

Figure 6. Estimated Distribution of Distillate Production from Wyo-3
Coal and A-6 Shale Oil at Low and High Severity Reaction
Conditions

The Roles and Importance of Hydrogen
Donation and Catalysis in Coprocessing

Christine W. Curtis, Frankie N. Cassell,
and Donald R. Cahela

Chemical Engineering Department
Auburn University, Alabama 36849

The roles and relative importance of hydrogen donation and catalysis in producing an upgraded product slate from coprocessing are explored. These effects are examined in two types of systems: the upgrading of residuum and the coprocessing of coal with residuum. In these experiments, the reactions were performed both thermally and catalytically in the presence and absence of tetralin (TET) to elucidate possible synergetic interactions between the catalyst and TET for increased coal conversion and an improved product slate.

Catalytic coprocessing which has been extensively reviewed by Monnier (1) generally produces an improved product slate and a higher degree of upgrading than does thermal coprocessing. Previous work performed by Curtis et al. (2,3) has shown the necessity of having highly accessible catalysts for coprocessing. Catalyst accessibility affects both the amount of coal conversion and the degree of upgrading of liquefied coal to soluble products and of petroleum asphaltenes to pentane solubles. In this work, two highly accessible catalysts are investigated: an oil soluble catalyst, Mo naphthenate, and a presulfided commercial NiMo/Al$_2$O$_3$ hydrotreating catalyst which was ground to -200 mesh to increase its accessibility and, hence, its activity. Mo naphthenate is a metal salt of an organic acid that is thought to be converted to an active catalyst under typical coprocessing conditions of high temperature and hydrogen atmosphere with a partial pressure of hydrogen sulfide. The active species is believed to be a noncolloidal metal sulfide (4,5).

The effect of hydrogen donor compounds on the products obtained from coprocessing has been examined by Curtis et al. (6). They concluded that hydrogen must be available for upgrading reactions to occur in coprocessing and that the hydrogen can be present either as molecular H$_2$ or donable hydrogen. The type of donor present affected the product slate; tetrahydroquinoline promoted coal conversion while tetralin and dihydrophenanthrene promoted the production of lighter products. When reacted in either a H$_2$ or N$_2$ atmosphere, concentrations of donable hydrogen at the 0.5 wt% level or higher were required to substantially affect coal conversion.

The objective of the current work is to investigate the effect of hydrogen donor addition in conjunction with catalytic hydrotreatment on the products obtained from upgrading residuum and coprocessing coal with petroleum residuum. The reaction products are evaluated in terms of solubility fractions, coal conversion to solubles in the solvent extraction scheme used and oil production. Oil production is defined as the amount of pentane solubles after reaction minus the initial pentane solubles divided by the upgradeable materials which are the pentane insoluble materials from maf coal and the residuum. In addition, the amount of hydrogen transferred to the products via gas-phase molecular hydrogen and donation by hydrogen donors is examined. The efficacy of donable hydrogen in promoting coal conversion and producing a high quality product slate is evaluated in thermal and catalytic coprocessing.

Experimental

Upgrading and Coprocessing Reactions. Upgrading and coprocessing reactions were conducted in 50 ml stainless steel reactors, charged with 1250 psig H_2 cold (giving ~3000 psi at reaction temperature), 3g mf coal and 6g solvent. In the catalytic experiments, the catalyst charge was 1g of presulfided Shell 324 $NiMo/Al_2O_2$ (0.044g Mo/g mf coal) ground to -200 mesh from 1/16" inch extrudates or, when using Mo naphthenate, the charge was 0.002g Mo/g mf coal. Reaction conditions were 30 minutes at $400^{\circ}C$ for the thermal reactions and at 400° and $425^{\circ}C$ for the $NiMo/Al_2O_3$ and Mo naphthenate reactions. The reactors were agitated at 700 cpm with 2 steel balls as agitation aids. Maya topped long resid (TLR) was used in the upgrading reactions and as the solvent in the coprocessing reactions. For coprocessing, Western Kentucky 9/14 bituminous coal was used. In the reactions using TET, one weight percent donable hydrogen was introduced; the TET composed about one-third of the solvent. Each upgrading or coprocessing reaction was, at least, duplicated and some were triplicated or quadruplicated. The activity of the $NiMo/Al_2O_3$ was tested by reacting naphthalene in H_2 at $300^{\circ}C$. Naphthalene (NAPH) was nearly totally hydrogenated forming TET and decalin (DEC), producing the expected amount (7). The activity of the Mo naphthenate was also tested using naphthalene hydrogenation.

Product Analysis. The liquid products obtained from the upgrading and coprocessing reactions were analyzed using solvent extraction. The product fractions obtained were **PS** - pentane soluble; **BS** - benzene soluble, pentane insoluble; **MCMS** - methylene chloride/methanol soluble benzene insoluble; **THFS** - tetrahydrofuran (THF) soluble, methylene chloride/methanol insoluble; **IOM** - insoluble organic matter, insoluble in THF. In the coprocessing reactions, coal conversion was calculated on the basis of the amount of material converted to soluble products and was corrected for the amount of IOM formed in the upgrading reactions with equivalent reaction conditions. The weight of the gas after reaction was measured and the hydrogen consumption was determined using PVT methods. The hydrogen consumption was calculated for each reaction.

The PS and BS fractions of the reaction products were analyzed by temperature programmed gas chromatography using a Varian Model 3700 equipped with a FID and a 60 m DB-5 J and W fused silica capillary column. The PS and BS fractions were analyzed for TET, DEC and NAPH to determine the amount of hydrogen transferred by TET to coal and the petroleum solvent. An internal standard, p-xylene, was used. Dihydronaphthalenes were not detected at detectability levels of 2.4×10^{-11}g.

Solvent extraction analysis of Maya TLR showed that the residuum before reaction was composed of 77.6% PS and 22.4% BS. TET, NAPH, and DEC were not observed in the chromatograms of the extracted residuum at the detectability levels of 2.4×10^{-11} g. Western Kentucky 9/14 coal was nearly insoluble at room temperature with less than 3% MCMS and 1% THFS being present.

Discussion of Results

Upgrading of Residuum. The results from the thermal and catalytic upgrading reactions performed in the presence and absence of tetralin are given in Table 1. After Maya TLR was thermally upgraded in H_2, the product solubility fractions obtained deviated only slightly from the unreacted residuum. The major change observed was the decrease of the BS fraction and the formation of lighter and heavier fractions. Hydrogen consumption during the reaction was 17.7 mmole of H_2 per 6 g charge of residuum. No TET, NAPH, or DEC was observed in the upgraded residuum. When TET was added at the one percent donable hydrogen level, the product analysis was similar to that without TET except that the IOM was greater

and the oil fraction was slightly less (Table 1). Both hydrogenation and dehydrogenation reactions involving TET were observed in the reaction system:

$$\text{TET} \longrightarrow \text{NAPH} + 2\text{H}_2 \qquad\qquad 1)$$
$$\text{TET} + 3\text{H}_2 \longrightarrow \text{DEC} \qquad\qquad 2)$$

The dehydrogenation reaction was predominant and produced H_2 while the hydrogenation reaction occurred to a lesser extent and consumed H_2. The net amount of hydrogen transferred was calculated by subtracting the H_2 consumed by reaction 2 from that produced from reaction 1.

Table 1
Upgrading of Residuum

Product Distribution, %	Thermal 400°C Maya TLR	Thermal 400°C Maya TLR + TET	NiMo/Al$_2$O$_3$ 400°C Maya TLR	NiMo/Al$_2$O$_3$ 400°C Maya TLR + TET	NiMo/Al$_2$O$_3$ 425°C Maya TLR	Mo Naphthenate 400°C Maya TLR	Mo Naphthenate 425°C Maya TLR	Mo Naphthenate 425°C Maya TLR + TET
Gas	1.9	2.0	2.1	2.4	3.7	1.3	2.7	1.7
PS	80.0	79.1	85.4	88.1	86.0	80.5	86.7	85.2
BS	17.1	17.4	7.7	5.3	4.5	15.9	9.9	11.0
MCMS	0.4	0.3	0.7	1.2	0.4	0.6	0.2	0.9
THFS	0.5	0.4	0.7	1.1	0.2	0.2	0.1	0.6
IOM	0.1	0.8	3.4	1.9	5.2	1.5	0.4	0.6
$H_{2(g)}$ Consumed, mmoles	19.5	14.2	31.3	28.5	44.3	23.1	19.5	12.82
H_2 Transferred, mmoles	NA*	2.6	NA	0.5	NA	NA	NA	0.62
Total H_2 Used, mmoles	19.5	16.8	31.3	29.0	44.3	23.1	19.5	13.44
Oil Production, %	11.4	10.2	39.6	53.5	44.1	16.0	43.6	39.5

NA: Not Applicable

In the thermal upgrading reaction with TET, 2.6 mmoles of H_2 were transferred from TET to the residuum and an average of 14.2 mmoles of molecular hydrogen were consumed; therefore, the total hydrogen utilized by the residuum was 16.8 mmoles. Although the total amount of H_2 transferred to and consumed by the residuum was greater in the reaction without TET, the increased hydrogen utilization by the residuum did not result in higher conversion of BS to PS; both reactions had nearly equivalent oil production.

Catalytic Upgrading. In the catalytic upgrading of Maya TLR with NiMo/Al$_2$O$_3$, two-thirds of the original BS were reacted, forming both lighter and heavier products (Table 1). A substantial amount of IOM, 3.4%, was produced compared to 0.1% in the thermal reaction. Catalytic hydrotreatment increased oil production to ~ 40% compared to 11.4% in the thermal reaction and hydrogen consumption was doubled. With NiMo/Al$_2$O$_3$, trace but measurable quantities of DEC, TET, and NAPH were observed in both the PS and BS product fractions. These results indicate that while substantial upgrading, i.e., high oil production and hydrogen consumption, occurred, coking also occurred, producing heavy products from the residuum.

In Table 2, the hydrogen contents of the PS and BS fractions from the upgrading reactions are given. Comparing the hydrogen content obtained from

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catalytic to the thermal hydrogenation shows increases in the hydrogen content in both PS and BS fractions with NiMo/Al$_2$O$_3$. Thus, it appears that the increased hydrogen consumption resulted in a direct increase of the hydrogen content of the products. Comparison of the gas chromatograms obtained from both the PS and BS fractions prior to the reaction to that obtained after the thermal and catalytic reactions, however, did not show any visible changes in the product fingerprint. Changes in the compounds present or the addition of new compounds to these product fractions was not discernible in the chromatograms.

Table 2
Elemental Composition of PS and BS Fractions from Upgrading Fractions

Reactants	Temperature °C	Catalyst	PS % C	PS % H	BS % C	BS % H
Maya TLR	No Reaction		84.7	11.5	NM*	NM
			84.7	11.4	NM	NM
Maya TLR	400	None	85.7	11.2	82.8	7.0
			85.6	11.4	83.1	7.0
Maya TLR	400	NiMo/Al$_2$O$_3$	87.1	12.0		
			86.8	11.8	83.9	8.5
Maya TLR	400	Mo Naphthenate	84.9	11.3	82.7	6.5
			84.6	11.2	82.9	7.6
Maya TLR	425	Mo Naphthenate	86.1	11.8	85.3	7.4
			88.0	12.1	85.3	7.3
Maya TLR + TET	No Reaction		86.9	10.0	NM	NM
Maya TLR + TET	400	None	86.6	10.2	83.6	7.3
			86.7	10.3	83.6	6.8
Maya TLR + TET	400	NiMo/Al$_2$O$_3$	87.9	10.9	79.3	8.7
			87.6	10.8	78.2	8.4
Maya TLR + TET	425	Mo Naphthenate	86.8	10.3	84.9	7.3
			87.0	10.3	84.3	7.4

*NM: Not measured

When TET was added, a higher oil production (53.5%) and a decrease in BS were observed, although the total amount of heavy products (MCMS, THFS, and IOM) was similar to the reaction without TET. In these reactions, the catalyst and TET were both positive factors in producing PS materials. The molecular hydrogen consumed by the residuum was nearly equivalent to the reaction without TET. Only 0.39 mmoles of NAPH were produced which was approximately one-sixth that produced in the thermal reaction, indicating that hydrogenation of NAPH formed during the reaction to TET occurred in the presence of NiMo/Al$_2$O$_3$.

The catalytic upgrading reactions with Mo naphthenate were performed at 400 and 425°C. Compared to the thermal reaction, only a small change in product slate was observed with Mo naphthenate at 400 °C. At an increased reaction temperature of 425°C, the activity of the Mo naphthenate catalyst appeared to be enhanced since substantial increases in the upgrading of Maya TLR were observed; BS was converted to PS and only small amounts, <0.4%, of IOM were formed. An oil production of 43.6% was achieved yielding a substantial increase over that (16%) observed at 400°C. When TET was added, the product slate was very similar to that without TET although the total mmoles of H$_2$ utilized by the residuum was slightly less (Table 1). Only 0.44 mmoles of NAPH were produced, again indicating the rehydrogenation of NAPH to TET in the presence of Mo naphthenate.

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Coprocessing of Coal with Residuum. In thermal coprocessing, Maya TLR and Western Kentucky 9/14 coal were reacted in the presence and absence of TET at a one percent donable hydrogen level (Table 3). The reaction without TET achieved 47.9% coal conversion which was corrected to account for the IOM produced from the reaction using Maya TLR alone. The thermal coprocessing reactions utilized 12.3 mmoles of H_2 and achieved an oil production of 12.6%. When TET was added, coal conversion increased to 69.7%; however, oil production was lowered to 4.1%. Although the consumption of molecular hydrogen in the reaction with TET was ~2 mmoles less than in the reaction without TET, an additional 6.5 mmoles of H_2 was transferred from TET to the coal/petroleum system, yielding the total of 16.6 mmoles of H_2 utilized by the coal/residuum system. The increased H_2 utilization by the coal/residuum/TET system resulted in increased coal conversion and in the production of the heavier product fractions but not in increased oil production.

Table 3
Coprocessing of Coal with Residuum at 400^{0}C

| Product Distribution, % | Thermal | | NiMo/Al$_2$O$_3$ | | Mo Naphthenate |
	Maya TLR + Coal	Maya TLR Coal + TET	Maya TLR + Coal	Maya TLR + Coal + TET	Maya TLR + Coal
Gas	1.7	1.9	1.8	1.7	1.9
PS	53.2	48.3	63.6	60.1	54.7
BS	17.3	18.6	17.9	22.3	18.4
MCMS	5.8	9.9	3.1	5.5	8.6
THFS	5.9	9.0	1.6	1.9	8.6
IOM	16.1	12.3	12.0	8.5	7.8
$H_{2(g)}$ Consumed, mmoles	12.3	10.1	30.2	45.7	26.7
H_2 Transferred, mmoles	NA*	6.5	NA*	0.6	NA*
Total H_2 Used, mmoles	12.3	16.6	30.2	46.3	26.7
Corrected Coal Conversion, %	47.9	69.7	68.9	81.8	78.5
Oil Production, %	12.6	4.1	23.3	29.2	3.8
BS Production, %	5.6	12.9	7.7	22.1	9.7

NA: Not Applicable

Catalytic Coprocessing. Catalytic coprocessing of Western Kentucky coal with Maya TLR was performed in the presence of NiMo/Al$_2$O$_3$ and Mo naphthenate catalysts and also with and without TET. Analysis of the products achieved from these reactions are given in Tables 3 and 4. Catalytic treatment with NiMo/Al$_2$O$_3$ achieved 68.9% coal conversion which was greater than thermal coprocessing (47.9%) and nearly equivalent to thermal coprocessing with TET (69.7%). The oil production from catalytic coprocessing was more than double that of the thermal reactions with and without TET. In addition, higher hydrogen consumption and lower yields of the MCMS and THFS fractions were obtained, indicating a more highly upgraded product. The combined effect of hydrogen donation from TET and hydrotreatment from NiMo/Al$_2$O$_3$ synergetically promoted coal conversion since the addition of TET produced a higher coal conversion (81.8%) than did the catalyst alone (68.9%) or the thermal reaction with TET (69.7%). High quality products were produced during

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the reaction with oil production reaching nearly 30%, higher BS and lower levels
of MCMS and THFS fractions were also observed. A higher consumption of molecular
hydrogen occurred with TET addition than without. During the reaction, three
times more NAPH was produced than DEC; however, the NAPH production of 0.53 mmoles
in the catalytic reaction was low compared to 3.4 mmoles produced in the thermal
reaction. As in the upgrading reactions, the presence of $NiMo/Al_2O_3$ caused NAPH to
be rehydrogenated to TET and a consumer of H_2. The total amount of H_2 utilized by
the coal/resid/TET system was 46.3 mmoles which was higher than the thermal
reaction or the $NiMo/Al_2O_3$ reaction without TET. A small increase in the
hydrogen content of the PS was observed compared to the thermal reaction as shown
in Table 5.

Table 4
Coprocessing of Coal with Residuum at 425°C

Product Distribution, %	Thermal Maya TLR + Coal	$NiMo/Al_2O_3$ Maya TLR + Coal	Mo Naphthenate	
			Maya TLR + Coal	Maya TLR + Coal + TET
Gas	4.1	3.5	4.0	3.6
PS	55.1	61.8	66.8	61.9
BS	15.0	19.8	19.3	21.8
MCMS	3.4	2.8	4.8	6.0
THFS	3.1	2.0	1.6	2.1
IOM	19.4	9.6	3.5	4.6
$H_{2(g)}$ Consumed, mmoles	29.8	41.6	57.5	49.9
H_2 Transferred, mmoles	NA*	NA	NA	2.6
Total H_2 Used, mmoles	29.8	41.6	57.5	52.5
Corrected Coal Conversion, %	52.4	80.6	89.5	89.3
Oil Production, %	6.6	22.8	31.4	32.0
BS Production, %	-1.8	11.3	12.6	19.5

*NA: Not applicable

When Mo naphthenate was used in coprocessing at 400°C, coal conversion
increased compared to the thermal reaction but little other effect was observed
(Table 3). When the temperature was increased to 425°C (Table 4), substantial
increases in coal conversion, hydrogen consumption, and oil production were
observed in the reactions using Mo naphthenate. Since in these reactions both a
catalyst was added and the temperature was increased, the effect of the
temperature increase on the reaction must be ascertained. This effect can be
evaluated from the data given in Table 4, by comparing the products produced
during the thermal reaction at 425°C to those produced with Mo naphthenate. Since
both coal conversion and oil production were low in the thermal reaction at
425°C, the high levels of coal conversion and oil production can then be
attributed to the catalytic activity of Mo naphthenate not the temperature
increase. Comparing Mo naphthenate to $NiMo/Al_2O_3$ at 425°C, shows that Mo
naphthenate is more active in terms of oil production and coal conversion even
though the concentration level of Mo in the $NiMo/Al_2O_3$ reaction was 22 times that
in Mo naphthenate reaction.

Reactants	Temperature °C	Catalyst	PS % C	PS % H	BS % C	BS % H
Maya TLR	400	None	84.5	11.4		
+ Coal			84.0	11.3	82.8	7.1
Maya TLR	400	NiMo/Al$_2$O$_3$	84.8	10.9	84.6	7.4
+ Coal			84.8	10.9	86.8	7.3
Maya TLR	400	Mo Naphthenate	84.3	10.8	83.6	7.2
+ Coal			84.3	10.8	84.1	7.2
Maya TLR	425	Mo Naphthenate	85.7	11.0		
+ Coal			84.6	10.6	86.3	6.4
			84.9	10.7	85.1	6.8
			85.1	10.6		
Maya TLR	400	None	86.3	10.1	83.8	6.9
+ Coal + TET			86.4	10.1	83.5	7.0
Maya TLR	400	NiMo/Al$_2$O$_3$	87.8	10.5		
+ Coal + TET			87.1	10.5	86.0	7.0
			85.7	10.3	84.7	7.1
			87.4	10.5		
Maya TLR	425	Mo Naphthenate	86.9	10.5	85.6	6.6
+ Coal + TET			86.5	10.3	85.7	6.6

The presence of TET in the coal/resid/Mo naphthenate system did not substantially change the product slate. Coal conversion, hydrogen consumption and oil production were the same as the reaction without TET. The total amount of NAPH formed during the reaction was 1.5 mmoles which fell between that for the thermal and NiMo/Al$_2$O$_3$ reactions. Ten times as much NAPH was formed as DEC. The H$_2$ utilized by the Mo naphthenate systems, 57.5 mmoles without TET and 52.5 mmoles with TET, was high compared to the other reactions performed. The product slates from these Mo naphthenate reactions show the effective utilization of H$_2$ in terms of coal conversion and oil production.

Effect of the Catalyst Compared to Tetralin on the Product Slate. The addition of catalyst in the residuum upgrading reactions increased the amount of oil production achieved and, in the case of NiMo/Al$_2$O$_3$, substantially increased the IOM formed. The presence of TET had varying effect; but only in the reaction with NiMo/Al$_2$O$_3$ did TET improve the oil production. In all upgrading reactions, the BS fraction was reduced during the reaction forming both lighter and heavier products. The catalytic reactions with NiMo/Al$_2$O$_3$ and Mo naphthenate at 425°C reduced the BS fraction the most. The combination of TET plus NiMo/Al$_2$O$_3$ resulted in the greatest reduction of the BS fraction and subsequent increase in the PS fraction.

In the coprocessing experiments, both the addition of catalyst and the addition of tetralin promoted coal conversion. For the NiMo/Al$_2$O$_3$ reactions, the combination of catalyst and tetralin synergetically promoted coal conversion. With Mo naphthenate, coal conversion was high (89.5%) without TET addition and no change was observed with the addition of TET. Thus, with a highly accessible and active catalyst, additional hydrogen donation from the solvent had little influence on coal conversion. Therefore, coal conversion in coprocessing appears to be dependent upon both catalyst and hydrogen donation except in the case of a highly active catalyst where catalytic activity predominates.

TET did not promote the production of PS materials in either the thermal or catalytic reactions. In fact, in the thermal reactions the presence of TET was detrimental to oil production.

The effect of TET and catalytic treatment on BS production is also instructive in examining the roles and relative importance of these two factors in coprocessing. BS production is defined as the difference between the final BS and the initial BS divided by the upgradeable material which is maf coal. Compared to the thermal reaction at 400°C, the addition of TET increased the amount of BS production (Table 3). Catalytic treatment at 400°C did not increase the BS production; however, the addition of TET to reaction system with $NiMo/Al_2O_3$ at 400°C did enhance BS production. At 425°C, the presence of $NiMo/Al_2O_3$ and Mo naphthenate increased the BS production as shown in Table 4. The addition of TET to the Mo naphthenate reaction again increased the BS production. Since all of these reactions showed positive oil production, the increases observed in the BS production were directly related to the upgrading of liquefied coal to BS products. Thus, the presence of TET assisted in the production of BS but not in the production of PS. The presence of a hydrotreating catalyst was required for oil production in the coprocessing reactions.

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Acknowledgments

REACTIVITY SCREENING OF FEEDSTOCKS FOR CATALYTIC COAL/OIL CO-PROCESSING

J. B. McLean and J. E. Duddy

Hydrocarbon Research, Inc.
(A Subsidiary of Dynalectron Corporation)
P. O. Box 6047
Lawrenceville, New Jersey 08648

ABSTRACT

HRI is currently conducting a four-party funded program to develop and demonstrate catalytic coal/oil co-processing using HRI's proven ebullated-bed reactor technology. The initial task in the research program was to determine reactivities of four coals (Illinois No. 6 and Ohio No. 5/6 bituminous, Alberta sub-bituminous and Texas lignite) and four petroleum residuums (Cold Lake, Maya, West Texas Sour, and Canadian IPL), both separately and in combination, using a 20cc microautoclave reactor. Experimental conditions and analytical procedures were developed to properly approximate ebullated bed conditions at the small, batch scale and to allow estimation of both coal and petroleum residuum conversions. Over 200 single-stage microautoclave tests were conducted studying severity, feedstock ratio, and catalyst effects. An interesting synergistic response was noted which indicates optimum performance at 50/50 coal/oil ratio for one particular feedstock pair. Initial results from a single-stage run in a continuous bench unit verified the trends noted in the microautoclave study.

INTRODUCTION

Hydrocarbon Research, Inc. (HRI) has developed and commercialized ebullated-bed reactor technology for the catalytic hydroconversion of both coal and heavy oil. The H-Oil® Process has been commercially demonstrated in both single- and two-stage process configurations, and the H-Coal® Process has been successfully scaled up through the 200 ton/day Catlettsburg pilot plant. While economic conditions have prevented the commercial appliction of direct liquefaction technology, coal/oil co-processing has gained increasing attention as a more commercially viable, nearer term way to introduce coal-derived liquid fuels into the market place. HRI's COILsm Process for co-processing was demonstrated on a bench unit scale as early as 1974[1], and more recently a two-stage process configuration was demonstrated on a Canadian feedstock combination of potential commercial interest[2]. In 1985, a four-party funded program was started to further develop and demonstrate catalytic coal/oil co-processing using HRI's ebullated-bed reactor technology. The program sponsors, objectives and elements are listed in Table 1. This paper focuses on the results of the microautoclave reactivity screening program.

MICROAUTOCLAVE DESCRIPTION AND PROCEDURES

With the recent increase in interest in co-processing, numerous investigators have reported results of batch reactor reactivity studies at various scales[3-6]. Many of these approaches tend to take a conventional coal liquefaction approach, by characterizing the effectiveness of petroleum oils as coal liquefaction "solvents". In coal/residuum co-processing, the oil is not a process solvent as such, but rather a reactant, and it's reactions/conversions are of equal - or even greater, depending on specific conditions - importance than those of the coal. The opposite approach to this is to view co-processing as an extension of refining technology, treating the coal as an additive, usually in limited quantities[7,8]. HRI's program was set up to consider a broad range of potential applications using catalytic ebullated-bed co-processing. The microautoclave experimental and analytical procedures were specifically developed to reflect this, and are in many respects considerably different than those used by other workers. Some discussion is therefore necessary to explain the basis for these differences.

The 20cc microautoclave reactor used in these studies is shown in Figure 1. Solvent, coal, residuum, and catalyst are charged batchwise in the appropriate amounts prior to mounting the reactor. Following pressure-testing, the desired H_2 (or N_2) pressure is established. Due to the volume of gas lines above the reactor itself, it is essentially an "infinite source" hydrogen system, and no adjustment of operating pressure due to temperature is usually required. The entire assembly is shaken vertically with approximately one-inch strokes at 460 rpm, with temperature control by immersion in a fluidized sand bath heater. Dual sand baths are available for simulation of two-stage, close-coupled processing. Two identical microautoclave reactors are always operated side-by-side. A cold trap is provided to collect any light liquids lost during operation or depressuring.

Following each run the reaction is quenched by immersion in a water bath, and slowly depressured. The reactors and cold traps are then removed, and the products are combined and subjected to the workup procedures described in Figure 2. The use of the catalyst basket allows separation of product solids from catalyst extrudates. Ash-balancing then allows calculation of coal conversion. If necessary, product ashes can be checked for catalyst metals to distinguish coal ash from attrited catalyst. TGA simulated distillation is used to estimate product residuum contents and calculate residuum conversions. For selected runs, solvent precipitation was used to calculate asphaltene and preasphaltene components in the product residuum, although this is of lesser utility in co-processing than in coal liquefaction since petroleum residua contains very low levels of insolubles.

As noted above, HRI's microautoclave operating procedures and conditions are specifically designed to most properly approximate the conditions of an ebullated-bed reactor, and are in many cases quite different than those "typically" used in the industry. Some specifics include:

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- **Catalyst Type and Loading** - The ebullated-bed reactor operates with conventional extrudate catalysts at very high loadings (up to 50% of the reactor volume is occupied by catalyst). Our microautoclave experiments typically charged a catalyst/feedstock ratio of 1/1 to reflect this. Techniques such as grinding of catalyst are not representative. The catalyst used typically is process-presulfided in a pilot unit, and the use of the catalyst basket allows separation from reaction products. Some assumptions are necessary in calculation procedures to account for items such as IOM deposition on catalyst, catalyst attrition, etc. during an experiment.

- **Feedstock Dilution with Distillate Products** - The ebullated bed is a well-mixed reactor, due to the typically high ratio of internal recycle to fresh feed. As a result, reaction occurs in a concentration represented by the products. No batch reactor can properly model a CSTR from the standpoint of fundamental kinetics, so a compromise has to be made. Since the initial conversion reactions in coal liquefaction are critical, an attempt is made to simulate the reactor environment in which they occur. Thus, microautoclave reactor charges are made up with a high level of distillate diluent. An attempt is made to approximate, to the extent possible, the properties of the distillate materials which would be expected to be produced from the feedstocks and conditions of interest. The distillate solvents used are generally materials produced in substantial quantities from larger pilot plant operations on the feedstocks of interest.

- **Product Analyses** - Coal conversion to THF-solubles is calculated in a fairly typical manner. As noted above, conversions based on solubilities in other solvents are not considered to be especially meaningful for co-processing. A simulated distillation procedure was developed using a Perkin-Elmer TGS-2 Thermogravimetric Analyzer (TGA), which allows estimation of $975°F^+$ conversions. No attempt is made to generate data such as gas yields or distillate product distribution or quality. Such data are difficult to generate reliably on such a small scale. Even if this could be done, the results would not be meaningful for scaleup due to the large impacts of the distillate diluents and the major differences between batch and continuous units, on any scale.

SCREENING STUDY CONDITIONS

A five-point, low-to-mild severity condition matrix was used to screen each feedstock and combination of interest, as shown in Table 2. As noted, a 4/1/1 charge ratio of distillate solvent/reactant (coal and oil)/catalyst was used. Severities ranged from 2-20 STTU, based on HRI's conversion model developed for coal conversions. It is recognized that the time/temperature relationships for co-processing may not be truly represented by the STTU model, but it was used as a convenient way to express both severity parameters. The matrix used provides a comparison of three residence times at one temperature (800°F), and three temperatures at one residence time (30 minutes). All severities are lower than those typically encountered in larger scale operations. This serves to keep conversions low enough so that kinetic reactivity differences can be properly observed.

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FEEDSTOCK PROPERTIES

Some properties of the four coals and four oils studied are listed in Table 3. The Cold Lake feedstock was available as a deep-cut ASB from previous HRI H-Oil® studies, while the other three oils were provided as crude oils and were batch vacuum-distilled to approximately the same residuum content prior to the reactivity studies. All four coals were subjected to standard HRI bench unit preparation procedures (crushing, pulverizing to -70 mesh, drying to 2-10% moisture, and screening) and were further vacuum dried immediately prior to microautoclave testing. Three diluent solvents were also used, as shown. The Illinois-derived solvent was used for Ohio and Illinois bituminous coals, the Wyodak solvent for Alberta sub-bituminous coal and Texas lignite, and the Cold Lake solvent for all petroleum oils. Except for a few solvent-specific runs, solvents were blended in the same ratios as the feedstocks for each run.

PROGRAM OUTLINE

Over two hundred tests were conducted under the program, as noted in Table 4. The co-processing feedstock pairs chosen for evaluation were based on program sponsors' concerns and represent meaningful commercial candidates. No work was done on the Illinois No. 6 coal, since it was being extensively studied in HRI's parallel DOE funded coal liquefaction program. Most of the discussion to follow centers on the Ohio coal/Cold Lake ASB pair, which was the most extensively studied in 1985 (including both single- and two-stage process variable studies in the continous bench unit). This combination has been selected by OOSFC as the basis for a prototype commercial facility to be located in Ohio.

INDIVIDUAL FEEDSTOCK REACTIVITIES

Figures 3 and 4 show STTU response curves for the Ohio coal and the Cold Lake ASB. Similar curves were generated for each of the other feedstocks. In order to provide a quantitative reactivity ranking, kinetic rate constants were back-calculated from the data assuming various batch reactor models. For the oils alone, a second order fit was found to be the most satisfactory, as shown in Figure 5. While it is unlikely that the conversion reactions are truly second order, in the sense of being bimolecular, such a model fit is not unusual in systems of this type, where the "reactant" is not a single component but rather a range of components with different reactivities. For the coals, a more complex model would be required to separate the effects of coal conversion to THF-solubles, the fraction of converted coal which forms $975°F^+$ residuum, and the kinetics of conversion of the residuum. Realizing these deficiencies, the coal data were force-fit to the same simplified second order $975°F^+$ conversion model so that a direct comparison of oils, coals, and co-processing pairs could be made. These results are shown in Table 5. As expected, the oils are considerably more reactive to total $975°F^+$ conversion at low severities than the coals. It is notable that the co-processing pairs do not necessarily fall in either the order or magnitude which would be expected from the individual feedstocks, indicating that synergistic interactions do occur. It is also notable that the feedstock pair (Ohio/Cold Lake) studied most extensively in the

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program does not represent the "best" choice based on reactivities, but was chosen based on commercial considerations.

OHIO COAL/COLD LAKE ASB CO-PROCESSING

Figure 6 shows the reactivity curves for a 50/50 blend of Ohio coal and Cold Lake ASB. The drop off in 975°F$^+$ conversion at 20 STTU may be indicative of some regressive reaction due to poor solvent quality, as this is the highest temperature point (825°F) in the grid. The STTU axis has been extended to include a point at a typical bench unit operating severity. It is notable that there was no problem in achieving high (90% plus) coal conversion to THF solubles. This was true of all the pairs studied, indicating that the inherently poor hydrogen donor properties of the petroleum oils can be overcome by catalytic, ebullated-bed co-processing.

Figure 7 shows the effect of coal to oil ratio on conversions in a low severity test (10 STTU). As expected, the THF conversion increases as the coal concentration increases, since a higher percentage of the solvent is then coal-derived as well. The 975°F$^+$ conversion response is far less explainable. The individual feedstock points at 0 and 100% are connected, to represent expected conversions based on strict linear averaging. At coal concentrations up to 50%, conversions near or above this line occur, indicating a positive synergy. Surprisingly, at coal concentrations of 67-75%, a large negative interaction occurs, and 975°F$^+$ conversions are actually lower than those for coal alone. Each of these points was found to be reproducible. The most likely explanation for this phenomenon is that the presence of the petroleum oils sufficiently reduces the solvent quality in this range to cause a large drop in the conversion of the coal residua. At the lower coal concentrations, this effect is offset by the improved conversions of the petroleum residua. Interestingly, this effect shows itself only in the 975°F$^+$ conversions and not in the THF conversions. It should be noted here that coal/oil ratio studies with other feedstock pairs do not show this same negative behavior (at least not to this extent), but in all cases the response is non-linear.

Since this trend was interesting and unexpected, it was decided to repeat the coal/oil ratio studies at a higher severity, typical of bench unit process conditions. This was done to coincide with the single-stage bench run, which provided comparative results in the single-stage, integrated bench unit at 33, 50 and 67% coal. These results are shown in Figure 8. Note that the complex ratio response curve for 975°F$^+$ conversion has been reproduced, although the extent of the negative deviations at 67-75% coal are reduced. The bench unit data, at 33 and 50% coal, provide excellent agreement with the microautoclave data. The bench data at 67% coal do show some negative effect, althought not as pronounced as in the microautoclave. One key difference is that each bench data point represents several days of continuous, integrated operation with solvent quality equilibration, while microautoclave solvents are artificially composited. It should also be noted that the tie points at 0 and 100% coal were not determined on the bench unit, so that the extent of positive/negative synergy may not be directly comparable. The 50% coal case has been shown to be economically preferred at several severities at least in part due to synergistic reactivity effects.[9]

CONCLUSIONS

HRI's microautoclave has been shown to be an effective tool for comparing reactivities of coals, oils, and combinations for catalytic coal/oil co-processing. Specific improvements in experimental and analytical procedures were implemented to expand the utility of the microautoclave from coal liquefaction into oil and co-processing. Data generated on the Ohio coal/Cold Lake ASB combination led to some unexpected results, which were later confirmed by continuous bench unit studies.

ACKNOWLEDGEMENTS

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TABLE 1

HRI COAL/OIL CO-PROCESSING PROGRAM

SPONSORS: Electric Power Research Institute (EPRI)
             Ontario-Ohio Synthetic Fuels Corporation, Ltd. (OOSFC)
             Alberta Research Council (ARC)
             Dynalectron Corporation/HRI

OBJECTIVES:

1. Produce incremental liquid fuels from coal (including clean power plant fuels).

2. Upgrade (desulfurize, demetallize) poor quality residuum fuels.

3. Utilize chemically combined hydrogen from residuum to produce incremental liquid fuels from coal.

ELEMENTS (Laboratory):   Feedstock Characterization (ARC/HRI)
                         Microautoclave Reactivity Screening (HRI)
                         Batch Autoclave Screening (ARC)
                         Continuous Bench Unit Operations (HRI)

TABLE 2

MICROAUTOCLAVE STANDARD CONDITIONS
REACTIVITY SCREENING TESTS

8 gms solvent   Time, Temperature - Variable
2 gms reactant (coal plus oil)   2 gms pretreated catalyst (when used)
2000 psig hydrogen

Standard Solvent - H-Coal®/H-Oil® distillates
Solvents blended in same ratio as feedstocks

Severity - Standard Time Temperature Units
           1 STTU = 1 minute at 840°F

Severity Matrix

Temperature, °F	Time (Minutes)	STTU
750	30	2
800	15	5
800	30	10
800	45	15
825	30	20

TABLE 3

FEEDSTOCK PROPERTIES

OILS	COLD LAKE	IPL	MAYA	WEST TEXAS SOUR
Gravity, °API	6.9	14.5	4.1	14.7
Carbon, W %	83.2	87.2	83.1	86.5
Hydrogen, W %	10.2	11.0	9.7	11.4
Nitrogen, W %	0.5	0.4	0.7	0.3
Sulfur, W %	5.2	1.3	5.0	2.4
975°F+, W %	70.0	67.9	84.5	65.0

COALS	OHIO No. 5/6	ILLINOIS No. 6	ALBERTA SUB-BITUMINOUS	TEXAS LIGNITE
Proximate, W % Dry				
Volatiles	39.8	35.2	39.7	43.5
Fixed Carbon	53.4	52.8	52.1	44.5
Ash	6.8	11.7	8.2	12.0
Carbon, W %	75.3	69.9	67.9	63.3
Hydrogen, W %	5.6	4.9	4.7	5.3
Nitrogen, W %	1.6	1.4	1.4	1.2
Sulfur, W %	3.0	3.7	0.5	1.2
Ash, W %	6.8	11.7	8.2	12.0
Oxygen, W % (by difference)	7.7	7.8	17.3	17.0

SOLVENTS	H-COAL DERIVED Illinois	H-COAL DERIVED Wyodak	H-OIL DERIVED Cold Lake
Source			
Gravity, °API	11.5	15.8	24.4
Carbon, W %	89.3	89.4	86.0
Hydrogen, W %	9.4	10.1	11.8
Nitrogen, W %	0.5	0.3	0.2
Sulfur, W %	0.1	< 0.1	1.6
650°F+, W %	21.8	24.4	63.8

TABLE 4

PROGRAM SUMMARY

	NUMBER OF TESTS
Thermal Solvent Quality	21
Coal Reactivity - Ohio	12
Alberta	14
Texas	10
Oil Reactivity - Cold Lake	24
IPL	10
Maya	10
West Texas	5
Alberta/Cold Lake Co-Processing	18
Ohio/Cold Lake "	34
Ohio/Maya "	10
Ohio/West Texas "	10
Texas Lignite/W. Texas "	14
Hydrotreated Recycle Simulation	17
Two-Stage Simulation	8
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TABLE 5

REACTIVITY COMPARISON

Average Second Order Rate Constants for 975°F+ Conversion

OILS		CO-PROCESSING PAIRS (50/50 Ratio)	
West Texas	.44	Alberta/Cold Lake	.22
Maya	.31	Ohio/Cold Lake	.15
IPL	.24	Ohio/Maya	.32
Cold Lake	.14	Ohio/West Texas	.30
COALS - Texas Lignite	.20	Texas Lignite/West Texas	.29
Illinois No. 6	.12		
Ohio No. 5/6	.10		
Alberta	.08		

FIGURE 1

MICROAUTOCLAVE REACTOR

Thermocouple

Hydrogen
Inlet
and
Gas Outlet

Catalyst
Charge
Basket

MECHANICAL DESIGN

- 20cc Internal Volume
- Maximum Inlet Hydrogen Pressure 3000 psi
- Operations to Liquefaction Temperature
- Thermal and Gas Inlet Coupling
- 347ss Material of Construction
- External Cap Threads
- Reactor Cap Redesign
- Cold Traps
- Catalyst Basket
- Utilizes Whole Extrudate Catalyst

TESTING CAPABILITIES

- Thermal Tests Varying Charge,
  Feed Ratios, Temperature, Time

- Catalytic Tests Varying Charge,
  Feed Ratios, Temperature, Time

FIGURE 2

PRODUCT WORKUP PROCEDURES

```
          THF
      WASH REACTOR
          and
     CATALYST BASKET
            |
          SLURRY
            |
      THF FILTRATION
        |        |
     FILTER      |
      CAKE     FILTRATE
        |        |
       IOM    ROTO-EVAPORATE
       ASH        THF
        |          |
    CALCULATE     OIL  - - - - - ┐
   COAL CONVERSION    |           |
            TGA SIMULATED         |
             DISTILLATION      (OPTIONAL)
                 |               |
             CALCULATE           |
            975°F° CONVERSION    |
                        CHX/TOL
                      PRECIPITATION
                           |
                      CALCULATE OILS,
                 ASPHALTENES, PREASPHALTENES
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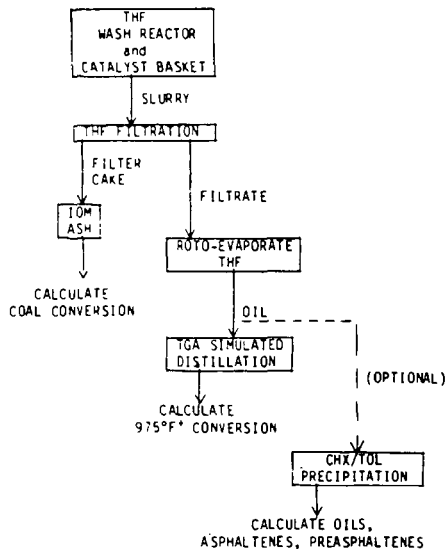
FIGURE 3

CATALYTIC REACTIVITY OF OHIO No. 5/6 COAL

+ THF Conversion
o 975°F$^+$ Conversion
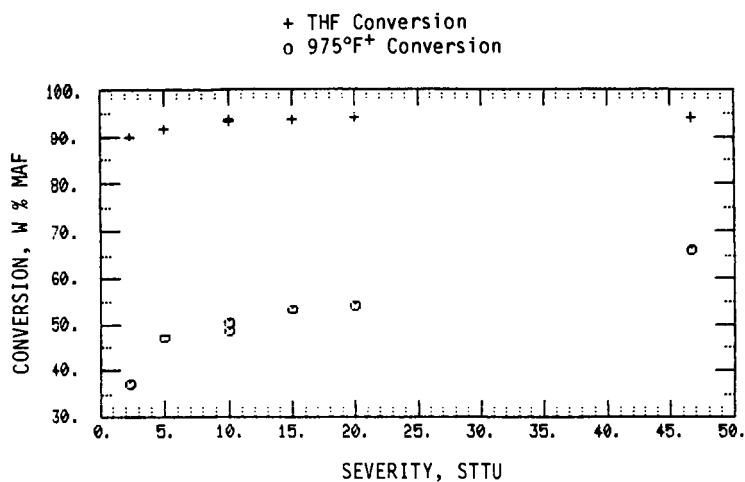
FIGURE 4

CATALYTIC REACTIVITY OF COLD LAKE ASB
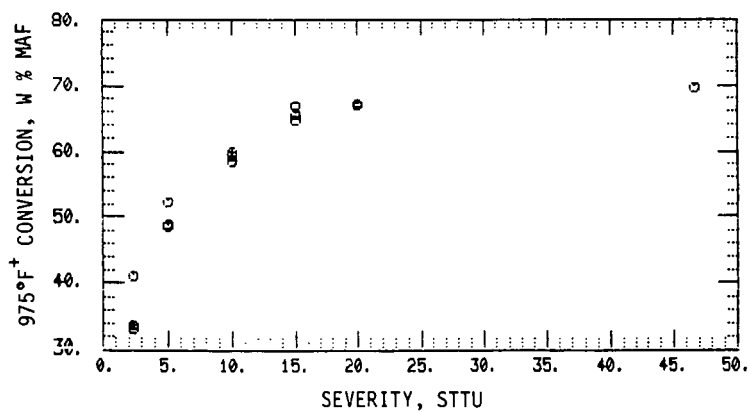
FIGURE 5

CALCULATED SECOND ORDER RATE CONSTANTS FOR
975°F⁺ CONVERSION OF OIL FEEDSTOCKS
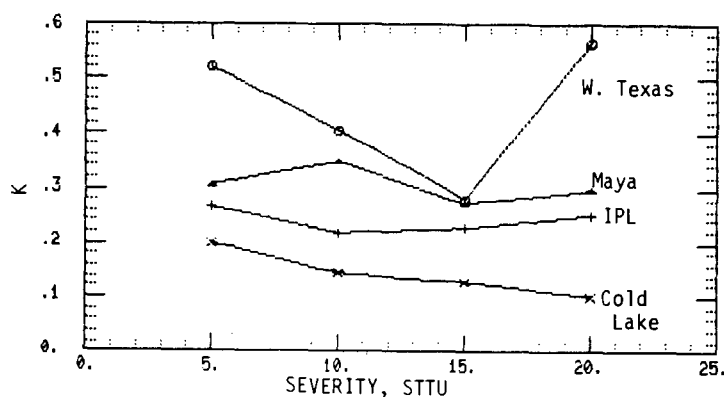
FIGURE 6

CATALYTIC CO-PROCESSING OF 50/50 BLEND OF
OHIO NO. 5/6 COAL AND COLD LAKE ASB

+ THF Conversion
o Total Feed 975°F⁺ Conversion

179
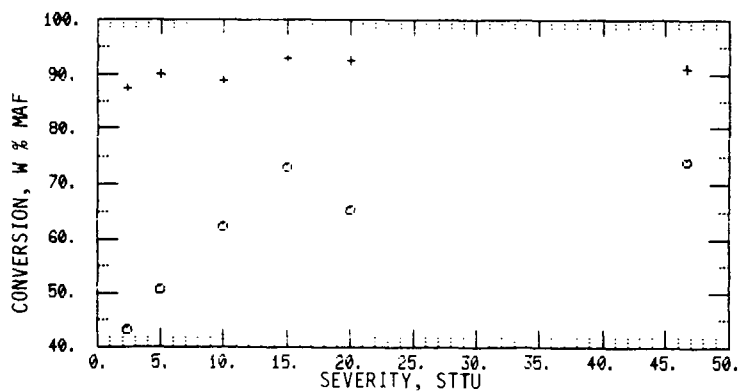
FIGURE 7

CATALYTIC CO-PROCESSING OF OHIO NO. 5/6 COAL AND COLD LAKE ASB
EFFECT OF COAL CONCENTRATION

(SEVERITY: 10 STTU)

+ THF Conversion
o Total Feed 975°F$^+$ Conversion
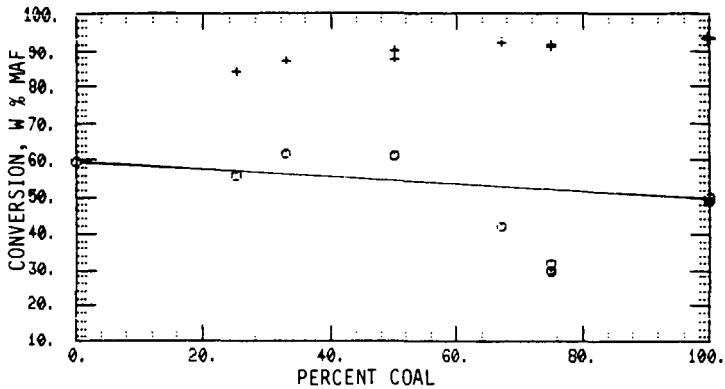
FIGURE 8

CATALYTIC CO-PROCESSING OF OHIO NO. 5/6 COAL AND COLD LAKE ASB
EFFECT OF COAL CONCENTRATION

(BENCH RUN SEVERITY)

+ THF Conversion
o 975°F$^+$ Conversion
x Bench Unit 975°F$^+$ Conversion Data

180
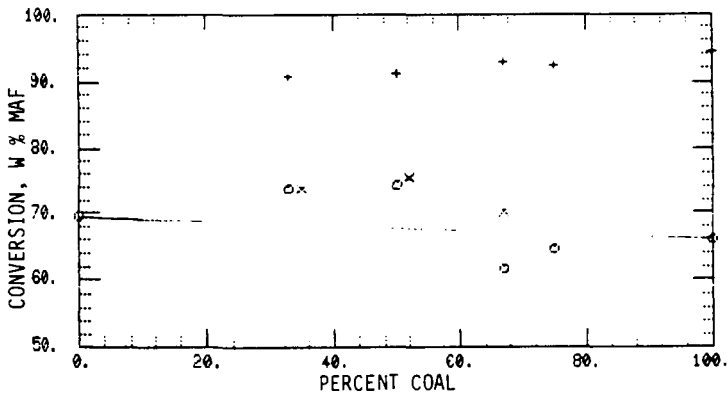
SINGLE-STAGE SLURRY CATALYZED CO-PROCESSING

John G. Gatsis

Signal Research Center Inc
Box 5016
Des Plaines, Illinois 60017-5016

INTRODUCTION

UOP Inc. and the Signal Research Center are currently engaged in a Department of Energy (DOE) sponsored program to determine if a slurry catalyzed, single-stage process involving the simultaneous conversion of coal and petroleum resid offers the potential for improved economics.

The program has been structured to accomplish the overall objectives of evaluating the technical feasibility and establishing a process data base on the Co-processing concept. Specific objectives include the establishment of overall criteria for the selection of coal type and petroleum characteristics, evaluation of process performance, and the cost estimation of a conceptual commercial facility.

This paper reviews results from the first phase of the program and early results from the continuous bench-scale unit currently in operation.

PROPOSED PROCESS CONCEPT

UOP Inc. and the Signal Research Center began development of the resid/coal Co-processing concept in 1970 and were issued a key patent in this area in 1972 (1). The information gained in this work plus the much longer and more extensive experience in petroleum resid upgrading and coal conversion were used to formulate a slurry catalyzed, single-stage process for the simultaneous conversion of coal and petroleum resid. This Co-processing process utilizes an active, well-dispersed catalyst and operates at relatively low temperatures. This allows high coal conversion without cracking of resid and coal to light gases, and minimizes thermal degradation reactions.

FEEDSTOCK SELECTION

Six vacuum resids, three bituminous coals and one subbituminous coal were selected for study.

The vacuum resids were selected based on their commercial importance (availability) and to provide a wide range of chemical and physical properties. These resids were vacuum fractionated to 510°C at the 5 vol-% point so that all would have similar boiling ranges, thus eliminating any process variations due to different amounts of vacuum gas oil (VGO) in the feedstock.

The chemical and physical properties are shown in Table 1. Figure 1 shows the relationship of API gravity with respect to hydrogen, C_7 insolubles and carbon residue content. The contaminants (C_7 insolubles and carbon residue) increase and hydrogen content decreases with decreasing API gravity.

The coal samples were selected primarily because of their use as references in other studies. The properties are shown in Table 2. The Wyodak Coal as received (C4.1) has a moisture content of 14.7 wt-%. It was dried in the laboratory to a moisture content of 1.78 wt-% (C4.2).

CATALYST COMPARISON STUDY

The premise of this work involves the concept that an active slurry catalyst will efficiently promote and effect the necessary dissolution and upgrading reactions as compared with a less active catalyst or a non-catalytic process, and thus maximize coal conversion and upgrading of the petroleum resid to produce a high quality syncrude.

Disposable, iron-based slurry catalysts, whose activities have been reported as being much lower than that of other metal slurry catalysts (2), have been shown to provide beneficial catalytic effects in the upgrading of coal and coal/resid mixtures (3,4). An iron-based slurry catalyst was tested to establish a comparison with the active UOP slurry catalyst. The iron-based disposable catalyst selected was a porous iron oxide (Fe_2O_3) from Kerr-McGee (5). A run was also made without catalyst.

Lloydminster vacuum resid (R4) and Illinois No. 6 coal (C1) were used as feed-stocks. The tests were conducted in an 1800 cc rocker autoclave. The equipment and procedure have been described in previous work (6). The operating conditions are shown below:

Resid/Coal Ratio	2
Pressure, psig	3000
Temperature, °C	Base
Residence Time, hrs	2

The iron-based catalyst was tested at twice the catalyst concentration of the UOP slurry catalyst to compensate for its lower anticipated activity with respect to the active UOP slurry catalyst.

The results of this catalyst comparison study are summarized in Table 3. The addition of either catalyst resulted in dramatic increases in coal conversion and heptane insoluble conversion but had little effect on the non-distillable con-version. The coal conversion and heptane insoluble conversion without the addition of catalyst was 66.6 wt-% and 21.3 wt-%, respectively. The coal conversion and heptane insoluble conversion increased to 80.5 wt-% and 63.9 wt-% with the iron catalyst and increased further with the UOP catalyst to 92.2 wt-% and 81.3 wt-%, respectively. The non-distillable conversion (510°C+) ranged from 69.3 to 73.6 wt-% for these three tests.

Although the iron oxide catalyst demonstrated some beneficial effects, its overall performance was inferior to the UOP slurry catalyst. The differences between these two catalysts becomes even more apparent when hydrogen consumption and product quality are also included as part of the evaluation. The product properties of the total liquid product for each catalyst system tested are summarized in Table 4.

The UOP slurry catalyst has the best hydrogenation capabilities of the three systems tested. The hydrogen consumption with the UOP slurry catalyst was 2.66 wt-%, compared to 1.84 wt-% and 1.68 wt-% using no catalyst and the iron catalyst, respectively. This higher hydrogen consumption yields a liquid product with the highest API gravity, highest hydrogen content and the lowest heptane insoluble con-tent. The higher API gravity product is important because although the product has the same boiling range as products derived from no catalyst and iron catalyst, it is less aromatic and more like petroleum fractions. Also, the lower heptane insoluble content means that the material would have a lower tendency to poison or foul con-ventional refinery upgrading catalysts, thus making it more economically attractive to upgrade.

COAL/RESID REACTIVITY EVALUATION

The reactivities of different coal/resid combinations were evaluated. All the vacuum resids were tested with one coal (Illinois No. 6, C1) and all the coals were tested with one resid (Lloydminster, R4). The subbituminous coal (Wyodak) was tested as received (14.7 wt-% moisture content, C4.1) and also dried (1.78 wt-% moisture content, C4.2). The tests were made at the operating conditions stated above with the UOP slurry catalyst.

Resid reactivity screening results are summarized in Figure 2. Coal conversions ranged from 87.9 to 92.5 wt-%. Hydrogen consumption generally decreased with increasing API gravity. The heptane insoluble and non-distillable conversions followed a similar trend.

Coal reactivity screening results are summarized in Figures 3 and 4. The three bituminous and the dried subbituminous (1.78 wt-% moisture content) coals showed no particular trends. MAF coal conversion and heptane insoluble conversion for each coal were similar. The subbituminous coal as received (14.7 wt-% moisture content), gave lower coal conversion (78.3 vs 90.3 wt-% for dried Wyodak) and lower heptane insoluble conversion (64.5 vs 78.8 wt-% for dried Wyodak).

CONTINUOUS BENCH-SCALE OPERATIONS

The objectives of the continuous bench-scale operations are to: 1) prove the process concept, 2) direct its development toward the goals of achieving maximum coal concentration in the resid/coal feed and producing the greatest distillate yield, and 3) establish a firm experimental basis on which to evaluate a conceptual commercial facility. The early work reported here has been directed at the first and third objectives.

A simplified block diagram of the pilot plant is shown in Figure 5. The slurry feed (finely ground coal, petroleum resid and catalyst) is combined with hydrogen-rich recycle gas and is then preheated before it enters the bottom of the upflow reactor. The products from the reactor are then separated into a gas and oil stream at the high pressure separator. The gas stream from the high pressure separator is combined with make-up hydrogen before being recycled back to the incoming fresh feed. The oil stream from the high pressure separator is sent to a stripper where the lighter hydrocarbons are separated from the heavier fraction. The lighter hydrocarbon stream is separated further in the debutanizer into C_4 minus and C_4 plus products. The heavier hydrocarbon stream from the stripper is sent to a vacuum fractionator to obtain appropriate fractions.

A temperature and space velocity survey was conducted processing Illinois No. 6 coal (C1.2) and a commercially fractionated Lloydminster resid (R8) with the UOP slurry catalyst. The commercially fractionated Lloydminster resid is lighter than the Lloydminster (R4) used in the autoclave studies, containing 15 vol-% more 510°C minus material. The tests were made at the operating conditions stated below. Three temperatures and three space velocities were run.

Operating Conditions

Resid	R8, Lloydminster Vacuum 8ottoms
Coal	C1.2, Illinois No. 6
Resid/Coal Ratio	2
Pressure, psig	3000
Temperature, °C	Varied
WHSV, G/Hr/cc	Varied

The effects of temperature on product distribution and conversions are shown in Table 5. The product distributions give the expected trends, an increase of lighter

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fractions and a decrease of heavier fractions with increasing temperature. Coal conversion and heptane insoluble conversion exhibited an interesting trend in the higher temperature range. At the lowest temperature, 83.0 wt-% of the MAF coal was converted. Coal conversion increased to 91.8 wt-% at the mid-temperature, and then decreased slightly to 90.7 wt-% at the highest temperature. Heptane insoluble conversion behaved similarly, increasing from 72.8 wt-% at the lowest temperature to 82.2 wt-% at the mid-temperature, then decreasing to 72.5 wt-% at the highest temperature. The fact that both coal conversion and heptane insoluble conversion decreased at the highest temperature suggests that the highest temperature is too severe, resulting in thermal degradation reactions. At lower temperatures, catalytic effects predominate over thermal effects.

The effects of residence time on product distribution and conversion are shown in Table 6. The product distributions show an increase of lighter fractions and a decrease of heavier fractions with longer residence time. However, coal conversion and heptane insoluble conversion show adverse responses to the longest residence time. At 1.01 WHSV (g/hr/cc reactor volume), 86.8 wt-% of the MAF coal was converted. Coal conversion increased to 91.8 wt-% at 0.78 WHSV, and then decreased slightly to 90.5 wt-% at the 0.62 WHSV. Heptane insoluble conversion behaved similarly , increasing from 75.7 wt-% at 1.01 WHSV to 82.2 wt-% at 0.78 WHSV, then decreasing significantly to 69.9 wt-% at 0.62 WHSV. Analogous to the high temperature experiment, both decreased coal conversion and decreased heptane insoluble conversion at the lowest space velocity suggest that too severe an operating condition, in this case residence time, is resulting in thermal degradation reactions.

CONCLUSIONS

The single-stage, slurry-catalyzed Co-processing concept was successfully demonstrated in laboratory batch experiments. The active UOP catalyst gave high coal conversion and high conversion to liquid product at relatively low temperature and, as a result, thermal degradation reactions and cracking of resid- and coal-derived liquid to light gases were minimized. The liquid hydrocarbon product is of high quality and can be efficiently utilized as a feedstock in existing refineries.

The continuous bench-scale operation gave similar performance to the laboratory batch experiments, satisfying the proof-of-concept objective. In addition, data generated to date initiate a firm experimental basis on which to evaluate a conceptual commercial facility. These data show that the Co-processing process is sensitive to high severity conditions (temperature, residence time). High coal conversion and high conversion to high quality liquid product can be achieved by operating at relatively mild conditions where thermal degradation reactions are minimized.

ACKNOWLEDGMENT

REFERENCES

1. J. G. Gatsis, U.S. Patent 3,705,092, "Solvent Extraction of Coal by a Heavy Oil" (1972).

2. S. W. Weller, "Catalysis in the Liquid Phase Hydrogenation of Coal and Tars," Ch 7 in "Catalysis," Vol 4, P. H. Emmett (ed) Reinhold, New York (1956).

3. F. Freidrich and B. Strobel, "Liquefaction of Coal in the Federal Republic of Germany," International Seminar on the Replacement of Fuels, University of Liege, May 25-27, 1981.

4. "Status of Synfuels Development in Japan," NEDO, Synfuels, 3rd Worldwide Symposium, Washington, DC, November 1-3, 1983.

5. A. S. Paranjape and D. E. Rhodes, "Use of Iron Oxide and Hydrogen Sulfide to Improve Integrated Two-Stage Liquefaction," Proceedings of DOE Direct Coal Liquefaction Contractors' Review Meeting, October 17-18, 1984.

6. J. G. Gatsis et al., "Coal Liquefaction Co-Processing," Proceedings of DOE Direct Coal Liquefaction Contractors' Review Meeting, November 19-21, 1985.

TABLE 1

Resid Name	U.S. Mid-Continent (R1)	Kuwait (R2)	Alaskan North Slope (R3)	Lloydminster (R4)	Hondo (R5)	Maya (R6)	Lloydminster (R8)
Total Sample							
API Gravity	12.70	7.90	8.90	3.60	3.70	2.80	6.50
Specific Gravity	0.9813	1.0151	1.0078	1.0474	1.0466	1.0536	1.0254
D-1160, °C							
IBP, vol-%	473.0	472.0	422.0	406.0	478.0	452.0	369.0
5	510.0	505.0	494.0	509.0	512.0	515.0	432.0
10	525.0	517.0	515.0	-	524.0	532.0	463.0
20	546.0	542.0	541.0	-	-	-	505.0
30	568.0	-	-	-	-	-	-
EP	568.0	556.0	550.0	509.0	524.0	532.0	523.0
Overhead, vol-%	30.0	26.0	24.0	6.0	10.0	10.0	26.5
Analysis, wt-%							
Carbon	87.30	84.15	84.10	82.70	81.20	83.90	83.70
Hydrogen	10.25	10.55	10.85	10.15	10.10	9.15	10.00
Oxygen	0.30	0.35	0.27	0.29	0.36	0.48	-
Sulfur	1.0	4.9	2.3	5.6	6.6	4.9	5.1
Nitrogen	0.45	0.35	0.55	0.62	1.10	0.71	0.48
Carbon Residue	16.50	18.00	17.30	22.20	19.90	26.10	17.30
Petroleum Ash	0.030	0.020	0.020	0.090	0.110	0.126	0.051
C_7 Insolubles	8.29	5.95	4.80	18.10	17.80	22.40	13.91
Nickel, ppm	35.0	28.0	38.0	122.0	157.0	116.0	83.0
Vanadium, ppm	113.0	100.0	79.0	278.0	435.0	595.0	165.0
Iron, ppm	62.0	4.5	2.0	82.0	42.0	29.0	3.6
Molecular Weight	839.0	1054.0	810.0	1444.0	1125.0	1015.0	255.0
Furol Visc., sec (121°C)	755.0	1016.0	1295.0	1921.0	1126.0	2217.0	266.1
Pour Point, °C	38.00	38.00	32.00	91.00	79.00	91.00	120.0
Salt, lb/1000 bbls	2.90	3.50	1.20	3.30	4.00	20.70	5.2

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TABLE 2

Coal Analyses

Coal Name	Illinois No. 6 (C1)	Kentucky No. 9 (C2)	Indiana No. V (C3)	Wyodak (As-Received) (C4.1)	Wyodak (Dried) (C4.2)	Illinois No. 6 (C1.2)
Ultimate Analysis, wt-%						
Ash	9.65	8.68	8.12	10.30	12.00	10.56
Carbon	68.60	71.95	69.70	54.70	63.01	68.77
Hydrogen	4.51	4.78	5.40	3.83	4.50	4.84
Nitrogen	1.39	1.54	1.42	0.69	0.90	1.37
Sulfur	3.04	2.97	4.28	0.99	1.08	3.34
Oxygen*	9.66	8.53	9.37	14.79	16.73	7.03
Proximate Analysis, wt-%						
Moisture	3.15	1.55	1.71	14.70	1.78	4.09
Ash	9.65	8.68	8.12	10.30	12.00	10.56
Volatile Matter	39.95	42.35	48.25	37.00	42.60	39.90
Fixed Carbon	47.25	47.42	41.92	38.00	43.62	45.45

*Difference

TABLE 3

Catalyst Comparison Study

Operating Conditions			
Catalyst Type	None	Fe_2O_3	UOP Catalyst
Concentration	0	2 x Base	Base
Performance			
Conversions, wt-%			
Coal	66.6	80.5	92.2
Heptane Insolubles	21.3	63.9	81.3
Non-distillables (510°C+)	69.3	73.6	72.1
Hydrogen Consumption, wt-%	1.84	1.68	2.66

TABLE 4

Catalyst Comparison Study
Total Liquid Product Properties

Catalyst Type	None	Fe_2O_3	UOP Catalyst
API Gravity at 15.6°C	9.3	8.5	13.3
Specific Gravity	1.0050	1.0107	0.9772
Carbon, wt-%	85.15	84.40	85.50
Hydrogen, wt-%	10.05	9.6*	10.30
Oxygen, wt-%	1.00	-	1.23
Sulfur, wt-%	2.75	2.30	2.10
Nitrogen, wt-%	0.60	0.90	0.73
Ash, wt-%	0.005	<0.001	0.003
Heptane Insolubles, wt-%	37.03	14.52	7.37
Carbon Residue, wt-%	14.6	16.5	15.1
Vanadium and Nickel, wt-ppm	19	9	23

*Estimated

TABLE 5

Continuous Bench-Scale Operations

Effect of Temperature

	Base - 7	Base + 6	Base + 11
Temperature, °C			
WHSV, G/hr/cc	0.81	0.78	0.79
Product Distribution			
Hetero Gases + H_2O, wt-%	7.3	8.9	6.7
Hcbn. Gas C_4-, wt-%	1.9	2.5	3.7
C_5^+ - 371°C, wt-%	26.1	38.0	42.6
371 - 510°C, wt-%	47.1	40.1	39.2
510°C +	13.7	10.1	7.0
MAF Coal	6.1	3.0	3.2
Total, wt-%	102.2	102.6	102.4
Conversions			
Coal, wt-% MAF Coal	83.0	91.8	90.7
C_7 Insolubles, wt-%	72.8	82.2	72.5
510°C+, wt-%	49.2	64.2	65.7
371°C+, wt-%	25.9	40.1	42.0
H_2 Consumption, wt-%	2.16	2.58	2.45

TABLE 6

Continuous Bench-Scale Operations

Effect of Residence Time

Temperature	Base + 4	Base + 6	Base +5
WHSV, G/hr/cc	0.62	0.78	1.01
Product Distribution			
Hetero Gases + H_2O, wt-%	6.3	8.9	8.4
Hcbn. Gas C_4-, wt-%	3.1	2.5	2.3
C_5 - 371°C, wt-%	42.0	38.0	31.1
371 - 510°C, wt-%	43.4	40.1	41.9
510°C +	4.1	10.1	13.9
MAF Coal	3.3	3.0	4.7
Total, wt-%	102.2	102.6	102.3
Conversion			
Coal, wt-% MAF Coal	90.5	91.8	86.8
C_7 Insolubles, wt-%	69.9	82.2	75.7
510°C+, wt-%	67.7	64.2	56.8
371°C+, wt-%	38.7	40.1	33.2
H_2 Consumption, wt-%	2.19	2.58	2.29

FIGURE 1

VACUUM RESID FEEDSTOCKS
COMPOSITION

FIGURE 2
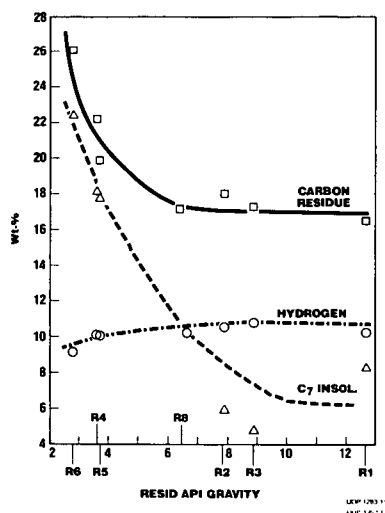
RESID REACTIVITY SCREENING
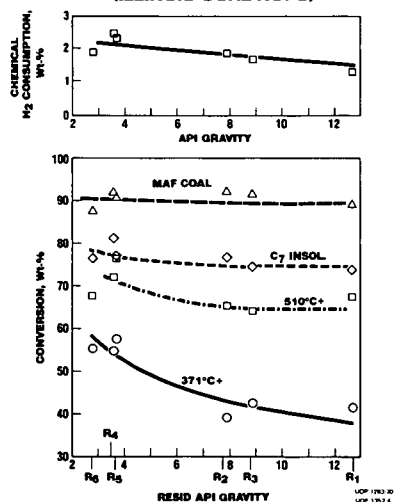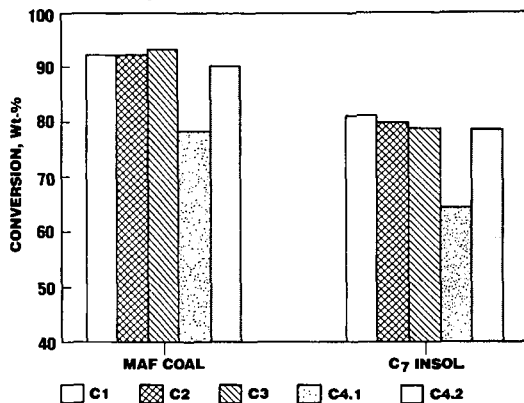## (ILLINOIS COAL NO. 6)

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FIGURE 3

COAL REACTIVITY SCREENING
(LLOYDMINSTER RESID)

UOP 1283-27
UOP 1352-5

FIGURE 4

COAL REACTIVITY SCREENING
(LLOYDMINSTER RESID)
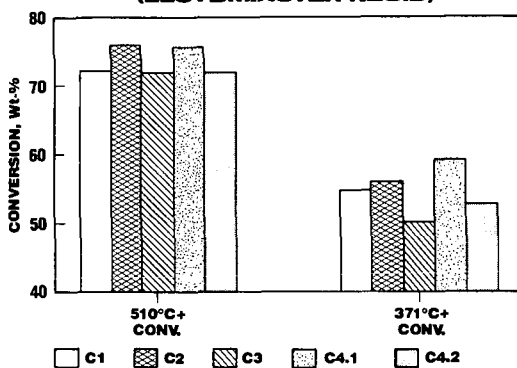
UOP 1283-31
UOP 1352-6

FIGURE 5
PILOT PLANT FLOW SCHEME

LEGEND
R = REACTOR
S = HIGH PRESSURE SEPARATOR
ST = STRIPPER
D = DEBUTANIZER
VF = VACUUM FRACTIONATOR
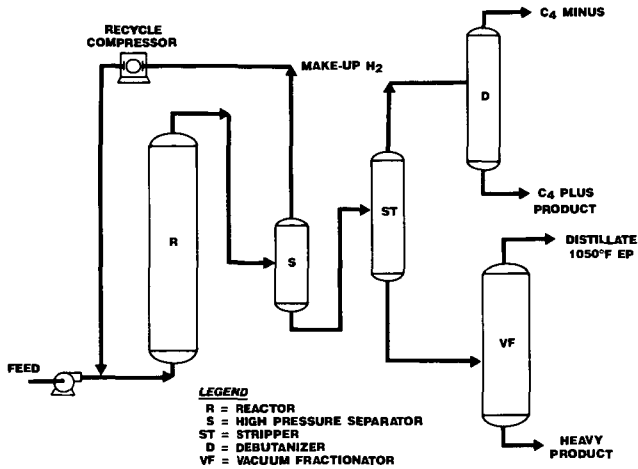
COPROCESSING USING H_2S AS A PROMOTER

P.M. Rahimi, S.A. Fouda and J.F. Kelly

CANMET, Energy, Mines and Resources Canada, 555 Booth Street,
Ottawa, Ontario K1A 0G1

INTRODUCTION

Coprocessing heavy oils, bitumens or petroleum residues with coal
can be considered as a bridge between coal liquefaction and
hydrocracking. The existing technologies of liquefaction and
hydrocracking can be applied with modification to coprocessing. In
terms of operation, coprocessing is less complicated than liquefaction
because recylce solvent is eliminated. Since the coprocessing solvent
is upgraded simultaneously with coal the reactor volume is utilized
more effectively. If residuum conversion levels during coprocessing
are as high as those in hydrocracking then coprocessing also offers a
significant saving in feedstock costs by substituting a significant
portion of the heavy oil with less expensive coal.

CANMET coprocessing involves the simultaneous upgrading of coal
and heavy oil or bitumen in a once-through mode of operation using a
disposable iron catalyst. The CANMET additive (pulverized coal
impregnated with iron sulphate), hereinafter referred to as $FeSO_4$, has
been identified as both an hydrogenation and coke-reducing catalyst.
Process feasibility has been investigated using a variety of coals and
heavy oils/bitumens(1). Also, it has been demonstrated that in terms
of product yields for subbituminous coals, CANMET coprocessing is
superior to liquefaction and is comparable to hydrocracking (2-3).

The effect of H_2S in hydrocracking of model compounds and in
liquefaction is well documented (4-11). The ability of H_2S to reduce
coke formation and increase liquid yield in coal liquefaction has been
patented by Exxon Research and Engineering Company (12). It has also
been shown that H_2S has benefical effects in non-catalytic crude oil
hydrorefining processes (13).

In a previous batch autoclave study the use of H_2S in
coprocessing subbituminous coal and bitumen resulted in high coal
conversion and distillate yield (14). The increase in product yields
in the presence of H_2S was attributed to its ability to donate its
hydrogen to radicals derived from coal and bitumen (15).

The objective of the present study was to verify the positive
effects of H_2S under coprocessing conditions using a continuous-flow
bench scale pilot plant and to compare the activity of H_2S with $FeSO_4$
under similar operating conditions.

EXPERIMENTAL

Process Unit

Coprocessing experiments were carried out in a 1-L
continuous-flow stirred tank reactor with a nominal capacity of 1 kg/h
of slurry feed while product samples were collected over 1-h periods
at steady state. For all the experimental runs reported in this
paper, the material balances were within ±5 wt %. For comparison
purposes, all the data were normalized to 100% material balance by
proportioning the losses over each of the product fractions. Other
details of the experimental unit are available elsewhere (2).

Feedstocks

The analysis of Forestburg subbituminous C coal and Cold Lake
vacuum bottoms (CLVB) is shown in Table 1. Additives or promoters
were $FeSO_4$ or H_2S or both. The H_2S was obtained from Matheson and
used as received. In experiments where H_2S was used it was pumped as
a liquid using a Waters LC pump model 6000A.

RESULTS AND DISCUSSION

Product Yields

Previous batch autoclave experiments indicated that H_2S is most
effective at low to moderate severities in terms of improving product
yields when compared to coprocessing without any additive. AT
moderate-high severity, using the feedstocks reported in this
paper, relatively high coke formation was observed even in the presence
of H_2S. For this reason, the CSTR experiments which involved H_2S only
were performed at low to moderate severities. For moderate-high
severity experiments, iron sulphate was used to assure smooth process
operation and to prevent coke formation. Attempts to perform
coprocessing experiments in the CSTR unit using CLVB and Forestburg
coal without any catalyst even at low severity resulted in coke
formation and plant shutdown. Thus, it is not possible to compare the
results of experimental runs using H_2S only with those using no
additive or promoter as was done in the batch autoclave studies (15).
The fact that coprocessing experiments could be performed in the CSTR
with H_2S and no other catalyst at low and moderate severities is
significant and verifies earlier batch results which indicated that
H_2S prevents coke formation under the conditions employed (14-15).

Table 2 compares coprocessing results obtained in the presence of
H_2S and iron sulphate at two levels of severities. At both levels
replacement of $FeSO_4$ with H_2S resulted in higher distillate yield,
pitch and coal conversions. The results of batch studies indicated

that product yields depend on H_2S concentration. At moderate
temperature maximum coal conversion and distillate yield were obtained
at about 3.5 wt % H_2S based on maf slurry feed (15). However, the
results reported in this work are based on only one experimental run
and are at approximately 8 wt % H_2S based on maf slurry feed. No
optimization of H_2S concentration on product yields was carried out in
this CSTR study.

The increase in conversions and distillate yield in the presence
of H_2S can be rationalized by its hydrogen-donor ability. Hydrogen
sulphide can donate its hydrogen directly to coal and bitumen-derived
radicals or the available hydrogens in H_2S can be transferred to
radicals via coal-derived liquids. The evidence for direct hydrogen
donation by H_2S comes from batch autoclave hydrocracking studies using
CLVB (14). At low severity, the presence of H_2S resulted in a
substantial improvement and at moderate severity a slight increase in
distillate yield. The considerable increase in distillate yield in
the presence of H_2S suggests that at least in part, hydrogen from H_2S
is transferred to bitumen-derived radicals. The previous study (14)
also showed that while the conversion of Forestburg coal in anthracene
oil increased with H_2S, distillate yield did not. However, in
coprocessing (batch and CSTR) both coal conversion and distillate
yield improved substantially when H_2S was used. These results may
indicate that H_2S promotes upgrading of bitumen during coprocessing.
An apparent synergism between coal and H_2S is also suggested by less
coke formation during coprocessing in the presence of H_2S relative to
the hydrocracking of bitumen only using H_2S as a promoter (15). Table
2 indicates that at least at low and moderate severities the
performance of H_2S under coprocessing conditions in a CSTR is as good
as or better than $FeSO_4$.

Table 3 compares the activities of iron sulphate with and without
H_2S. At very low and low severities addition of H_2S to $FeSO_4$ resulted
in an increase in coal conversions whereas distillate yields and pitch
conversions did not change. However, at moderate severity, H_2S had a
significant effect on distillate yield, coal and pitch conversions.
The presence of H_2S at moderate-high severity had small effect on
distillate yield and pitch conversion but no effect on coal
conversion. It appears that at higher severities the positive effect
of H_2S is masked by the presence of $FeSO_4$. A comparison of Tables 2
and 3 reveals that at low severity a higher distillate yield was
obtained with the H_2S only run. However, at moderate severity, no
improvement was observed using H_2S+$FeSO_4$ compared to H_2S only. Also,
the comparison clearly shows that at moderate severity coal conversion
in the presence of H_2S only (80.4 wt %) approaches that at
moderate-high severity using $FeSO_4$ only (86.3 wt %).

Product Characteristics

a) Distillates

Table 4 shows the characteristics of distillate products at four different severities and compares product qualities obtained in the presence of H_2S with those obtained using $FeSO_4$ or $H_2S + FeSO_4$. At very low severity it appears that the distillate products obtained using $H_2S + FeSO_4$ are relatively heavier than those obtained in the presence of $FeSO_4$ only. The sulphur content of the distillate did not change when H_2S was added to $FeSO_4$, however, the aromaticity increased from 26 to 31. This increase parallels that of increased coal conversion upon H_2S addition (see Table 3) and may imply that some coal-derived liquid contributed to the distillate. Again at low severity, higher coal conversion in the presence of H_2S only compared to $FeSO_4$ or $H_2S + FeSO_4$ resulted in a relatively heavier distillate. The sulphur content of the distillate decreased slightly in the H_2S only run. At moderate severity, the use of H_2S alone resulted in a heavier liquid product, lower H/C ratio and higher molecular weight than the distillate obtained using either $FeSO_4$ or $H_2S + FeSO_4$.

From the results shown in Table 4 it appears that the effect of $FeSO_4$ as a hydrogenation catalyst is more pronounced at relatively higher severities. At moderate severity, although similar coal conversions and distillate yields were obtained with both H_2S and $H_2S + FeSO_4$, a better distillate quality was obtained with $H_2S + FeSO_4$. Again the higher molecular weight in the H_2S only run may suggest that more coal-derived liquid contributes to the distillate but the product is not upgraded to the same degree as when $FeSO_4$ is used. The oxygen content of the distillate decreased when H_2S was used instead of $FeSO_4$. Addition of H_2S to $FeSO_4$ further reduced the oxygen content which indicates that H_2S reacts with the oxygen functionalities in coal. However, sulphur content of the distillate increased slightly in the presence of H_2S only. At moderate-high severity, the product quality improved slightly in the presence of H_2S in terms of higher H/C ratio, lower oxygen content, aromaticity and molecular weight.

b) Residues

The compositions of residues obtained under different process severities are shown in Fig. 1. At very low severity, the addition of H_2S to $FeSO_4$ resulted in slightly higher yields of asphaltenes, preasphaltenes and lower THF insolubles. At low severity, the lowest yield of THF insolubles was obtained with H_2S which reflects a higher coal conversion than the $FeSO_4$ and $H_2S+FeSO_4$ runs. Under these conditions, the relative yields of oils, asphaltenes, and preasphaltenes remained unchanged. At moderate severity, the residue in the $FeSO_4$ run contained more residual oil than the H_2S run. However, as shown in Table 2 the total distillate yield as well as the pitch conversion in the H_2S run are higher. This suggests that the upgrading of heavy material in coprocessing is more efficient using H_2S than $FeSO_4$ at least at moderate severities. Little or no change

occurs in the yields of asphaltenes and preasphaltenes at moderate severity using the different additives. At moderate-high severity, adding H_2S to $FeSO_4$ resulted in slightly higher pitch conversion and consequently lower residue yield (Table 3). The drop in residue yield is reflected mainly in lower preasphaltenes and asphaltenes yields.

The toluene insolubles of some of the coprocessing residues were also examined using optical microscopy. This technique, supplemented by semi-quantitative elemental analysis by scanning electron microscopy has shown that it is possible to distinguish the originality of coal-derived and bitumen-derived solids in coprocessing residues (16). At moderate severity, the toluene insolubles of the coprocessing residue obtained using H_2S contains 22.5 vol % coal-derived solids (altered coal or unreacted coal) whereas the residue from the $FeSO_4$ run contains 52.1 vol % coal-derived materials. These results are consistent with the higher coal conversion in the H_2S run relative to the $FeSO_4$ run. Also a small amount, (0.9 vol %) of anisotropic solids in both the H_2S and $FeSO_4$ runs was detected whereas none was detected in the H_2S + $FeSO_4$ run.

CONCLUSIONS

Hydrogen sulphide has been shown to be an effective promoter in achieving high coal conversions and distillate yields when coprocessing subbituminous coal with bitumen vacuum bottoms in a continuous-flow bench scale operation. Results indicate that, at least, at low and moderate severities of operation H_2S performs as good as or better than $FeSO_4$ in terms of product yields as well as qualities. However, at higher severities, $FeSO_4$ is superior to H_2S.

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Table 1

Analysis of Feedstocks

Forestburg Coal

Proximate analysis
(wt %, as received)

Moisture	19.7
Volatile	37.2
Fixed carbon	36.1
Ash	7.0

Ultimate analysis
(wt % DAF)

C	74.34
H	4.81
N	1.78
O	18.58
S	0.49

Cold-Lake vacuum bottoms

Specific gravity, 15/15°C	1.038
Pentane insolubles, wt %	23.8
Pitch content, wt %	83.2
Conradson Carbon, wt %	17.1

Elemental composition, wt %

C	83.34
H	9.69
N	0.45
S	5.84
O	0.68

Metals, ppm

V	235
Ni	93
Fe	18

Table 2

Comparison of the Effects of H_2S with $FeSO_4$

Severity	Low		Moderate	
H_2S (1)	no	yes	no	yes
$FeSO_4$	yes	no	yes	no
Distillate yield (2)	22.9	27.3	36.3	43.2
Coal conversion (3)	53.7	67.9	70.4	80.4
Pitch conversion (4)	15.8	20.3	34.1	42.5

(1) 8 wt %, based on maf slurry feed   (2) wt %, based on maf slurry feed
(3) wt %, based on maf coal,   (4) $\dfrac{\text{maf (+525 °C) in - maf (+525°C) out}}{\text{maf (+525°C) in}}$
    defined as THF solubility

Table 3

Comparison of The Effects of $FeSO_4$ and H_2S + $FeSO_4$

Severity	Very low		Low		Moderate		Moderate-high	
H_2S (1)	no	yes	no	yes	no	yes	no	yes
$FeSO_4$	yes	yes	yes	yes	yes	yes	yes	yes
Distillate yield (2)	15.8	16.5	22.9	22.9	36.3	42.1	60.9	63.1
Coal conversion (3)	27.4	41.1	53.7	61.3	70.4	83.7	86.3	85.9
Pitch conversion (4)	8.1	7.5	15.8	18.6	34.1	42.4	64.8	69.7

(1) 8 wt %, based on maf slurry feed   (2) wt %, based on maf slurry feed
(3) wt %, based on maf coal,   (4) $\dfrac{\text{maf (+525°C) in - maf (+525°C) out}}{\text{maf (+525°C) in}}$
    defined as THF solubility

Table 4

Distillate Characteristics

Severity	Very low		Low			Moderate			Moderate-high	
H_2S	no	yes	no	yes	yes	no	yes	yes	no	yes
$FeSO_4$	yes	yes	yes	no	yes	yes	no	yes	yes	yes
API[d]	15.2	13.3	17.0	15.9	15.8	22.4	19.8	22.9	25.4	25.9
H/C	1.59	1.53	1.56	1.57	1.54	1.62	1.58	1.63	1.58	1.62
N,wt %	0.26	0.37	0.39	0.41	0.41	0.44	0.47	0.43	0.50	0.50
S,wt %	3.15	3.11	2.98	2.83	2.98	2.30	2.44	2.27	1.64	1.69
O,wt %	0.89	1.30	1.28	1.23	1.31	1.40	1.28	1.02	1.46	0.85
$\overline{fa}$	26	31	29	28	30	25	29	24	30	·25
$\overline{Mn}$,g/mole	–	–	307	320	322	272	305	279	293	278

FIGURE 1   RESIDUE COMPOSITION
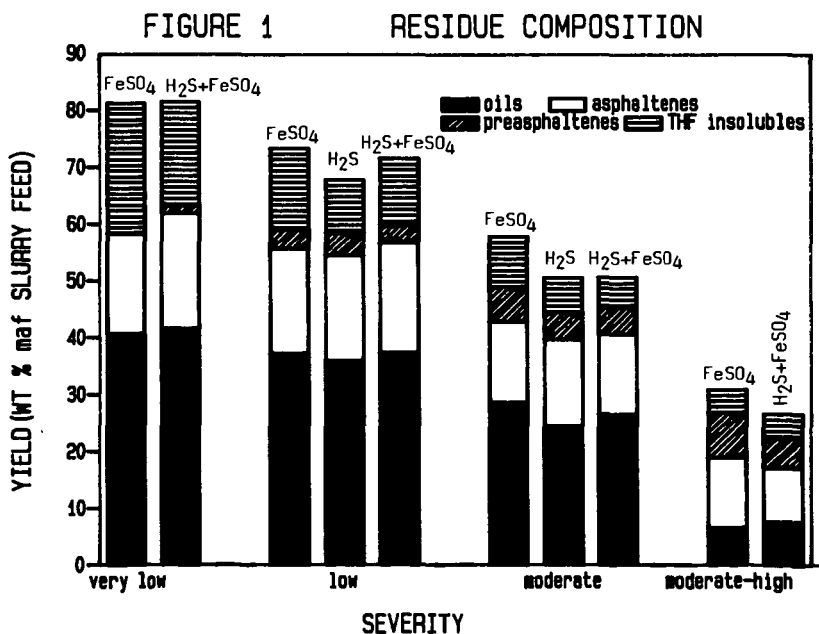
TWO-STAGE COPROCESSING OF SUBBITUMINOUS COALS AND BITUMEN OR HEAVY OIL*

B. Ignasiak, T. Ohuchi, P. Clark, D. Aitchison and T. Lee

Coal Research Department
Alberta Research Council
1 Oil Patch Drive
P.O. Bag #1310
Devon, Alberta, Canada
TOC 1E0

ABSTRACT

Pretreatment of subbituminous coal with an appropriately formulated mix of carbon monoxide and water, in presence of bitumen or heavy oil, results in very fast reactions characterized by a high degree of coal solubilization and deoxygenation. The reaction is catalysed by a mixture of alkali metal carbonates and proceeds readily at 380-400°C. The first-stage reaction product appears to be susceptible to further catalytic hydrogenation at 420-460°C with gaseous hydrogen yielding 65-70% (on daf feed) of hydrogen-rich distillable oil, composed mainly of naphtha and middle oil.

The process flowsheet is presented and the comparative economics of two-stage carbon monoxide/steam-hydrogen and hydrogen-hydrogen coprocessing schemes are discussed.

INTRODUCTION

Alberta is endowed with immense reserves of subbituminous coals (1), bitumen and heavy oil (2). The concept of coprocessing coal and petroleum derived solvents is not a new one (3,4) and there is a consensus that this approach is more attractive economically than conventional coal liquefaction (5). The most attractive feature of the coprocessing concept is its potential for elimination of oil recycle which may increase the output of the installation by up to three times.

It has to be emphasized that under Alberta conditions the economics of a coprocessing plant have to be compared to a heavy oil and/or bitumen hydrocracking plant. The major advantage of coprocessing as opposed to bitumen or heavy oil hydrocracking is the low cost of coal. This has to be weighed against the increased hydrogen consumption, increased plant complexity (conversion of coal to distillate oil requires more severe conditions compared to bitumen) and the element of risk associated with implementation of the new coprocessing technology.

A factor which may have a substantial effect on the economics of coprocessing as compared to bitumen or heavy oil hydrocracking is that of purely chemical nature. It has not been firmly established whether the interaction among coal- and bitumen-derived radical intermediates leads to an increase or a reduction in oil yield or its quality.

On the other hand, it has been demonstrated that hydrocracking of bitumen in a one-stage process in the presence of small (1-3% by weight) quantities of subbituminous coal results in significant improvement in oil yield (6). Similar results can be obtained by employing chars generated from brown coals (4,7) and this furnishes a strong evidence that catalytic effects and not the chemistry of the components of the substrate play a dominant role in a one-stage bituen

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hydrocracking process with low coal concentrations. However, the objective of coprocessing is to maximize the coal concentration in the feedstock without sacrificing the distillable product yield and quality.

The two-stage process developed at Alberta Research Council is based on solubilization of high oxygen subbituminous coal in bitumen (heavy oil) using a mixture of carbon monoxide/steam at 380-400°C in presence of alkali metal catalyst, followed by catalytic hydrocracking at temperatures of 420-460°C and pressures up to 18.0 MPa.

EXPERIMENTAL

The experiments were carried out in standard batch autoclave system and in a hot charge/discharge unit (a system developed for studying two-stage liquefaction processes).

Batch Autoclave Simulated Two-Stage Studies

The batch autoclave experiments were carried out in 1 litre magnedrive autoclaves (manufactured by Autoclave Engineers Ltd.) with internal cooling coils.

The coal/bitumen slurry was charged into an autoclave at room temperature followed by pressurizing the system with carbon monoxide (5.2 MPa) or hydrogen (8.3 MPa). The autoclave was heated up to 390°C, maintained at this temperature for 30 min, and depressurized at elevated temperatures. Gas samples were analysed using a CARLE gas chromatograph. The second stage (hydrogenation) catalyst and sulfur additive were then introduced to the cold reactor which was subsequently repressurized to 8.3 MPa with hydrogen. The reactor was heated to 440°C and held at this temperature for 60 min. Subsequently, the reactor was depressurized as before, cooled to room temperature and discharged. The product work-up procedure was the same as described before (8).

Hot Charge/Discharge Unit (HCDU)

The HCDU consists of two magnetically stirred reactors of one and two litre capacity and a high pressure vessel to collect the product slurry. The first reactor operates in batch mode and the second one in a semi-continuous mode. Details regarding construction and operation of the system were given elsewhere (8). The product work-up procedure and product analyses were the same as for batch autoclave tests.

DISCUSSION

Sufficient evidence has been accumulated to show that two-stage coal liquefaction process yields better results compared to conventional single-stage processes (9).

The importance of the first (solubilization) stage in the overall liquefaction process had been ignored until it became evident that depending on the results of the solubilization, the second (hydrogenation) stage proceeds more or less efficiently. Though no results of systematic research on the solubilization-hydrogenation relationship are available, one can speculate that the mechanism of the initial disintegration of coal and the character and properties of the intermediate soluble product may have a major influence on the effectiveness of the hydrogenation step.

The influence of solubilization of low rank coals on their hydrogenation may be particularly important due to their high oxygen content and high reactivity of a major fraction of this oxygen at temperatures significantly below the hydrogenation temperature. Presence of highly reactive oxygen in the coal may

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result in retrogressive reactions taking place during solubilization at higher temperatures. Therefore, for Alberta subbituminous coals a mixture of carbon monoxide/steam or hydrogen was tested in low temperature solubilization studies. The work carried out at Alberta Research Council on solubilization of indigenous subbituminous coals in CO/steam in bitumen and/or heavy oil showed that these coals are readily solubilized at a low temperature of 380-400°C with conversion 85-96% (10,11). Although the conversion was accompanied by low hydrocarbon gas generation and advanced deoxygenation for both gases tested (see Table 1), CO/steam appeared to be superior compared with hydrogen in terms of reaction kinetics measured as coal conversions at 390°C (see Table 2).

The susceptibility of the coal solubilized under mild conditions with either hydrogen or carbon monoxide/steam to further hydrogenation in presence of potassium molybdate is presented in Table 3.

Analysis of the results obtained in simulated two-stage autoclave experiments and presented in Table 3 indicates, that in terms of distillable oil yield the solubilization of coal in bitumen in presence of $CO/H_2O-K_2CO_3$ followed by catalytic hydrogenation yields slightly better results compared to solubilization in hydrogen and followed by catalytic hydrogenation. Furthermore, two-stage co-processing where solubilization was accomplished by action of either CO/H_2O or $CO/H_2O-K_2CO_3$ seems to result in somewhat lower generation of gaseous hydrocarbons compared to solubilization with hydrogen (Table 3). The coal conversion values are by far the highest (98%) for the sample solubilized using $CO/H_2O-K_2CO_3$.

In conclusion, on the basis of autoclave studies the two-stage $CO/H_2O-K_2CO_3$ - H_2 route appears to be marginally more appealing than the H_2-H_2 route in terms of product yields and conversion.

The Alberta Research Council route requires that CO be used as reducing gas in the first stage of the liquefaction process. It is noteworthy that the reforming technology for conversion of natural gas (CH_4) to either H_2 or CO is well known and in both cases is equally efficient in terms of the quantities of the reducing gas produced.

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad (1)$$

$$CH_4 + 3CO_2 \rightleftharpoons 4CO + 2H_2O \qquad (2)$$
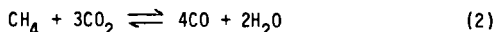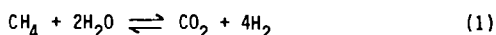
The conversion of methane to CO instead of H_2 is more attractive in view of the elimination of the demand for water and the potential for recycling the CO_2 produced in the first stage of the coprocessing. The disadvantage of reforming with CO_2 lies in endothermic nature of this reaction and in a need for separation of gases (namely CO, CO_2 and H_2).

The block diagram of the coprocessing plant based on the concept of $CO/H_2O-K_2CO_3$ - H_2 reaction is presented in Figure 1.

The process is composed of three trains: 1) distillation of bitumen and agglomeration of coal; 2) generation and separation of reaction gases; and 3) solubilization, hydrogenation, distillation and refining of volatile products.

Earlier work showed that bitumen based bridging liquid was very effective in removal of a major portion of mineral matter (particularly silica and clays) from subbituminous coals during their agglomeration (12). It is expected that deashing of coal may have a beneficial influence on liquefaction catalyst performance and resolve the problems associated with erosion of pressure let-down valves (13).

The overall mass balance of the optimized two-stage $CO/H_2O-K_2CO_3$ - H_2 coal/
bitumen process is presented in Table 4. The soluble extract ($+525°C$) accounts
for 12.3% of the feedstock (coal + bitumen) as compared with about 19% (see
Table 3) obtained from simulated two-stage autoclave tests. The reduction in
generation of extractable matter was achieved through more advanced hydrogena-
tion compared to autoclave tests. As a result the distillable oil yield after
optimization was increased to 70.1% (see Table 5) compared to 66.2% obtained in
an autoclave (Table 3). Equally important, the process generates mainly light
($-375°C$) oil, which accounts for about 90% of total oil produced. It is expec-
ted that in a continuous operation higher yields of distillable oils can be ob-
tained. Progress in development of an active, inexpensive and disposable
catalyst should have a major impact on further improvement of the ARC process
concept.

Recently completed economic feasibility studies on two-stage coal/bitumen
coprocessing (14) indicate that the Alberta Research Council concept to carry
out the solubilization stage in CO/steam atmosphere adds about $100 million to
the cost of the coprocessing plant and this accounts for approximately 8% of
total plant cost. However, when the feasibility studies were completed (early
1985) the data indicating that the $CO/steam-K_2CO_3$ solubilization results in
higher yield of distillable oils compared to hydrogen solubilization (see Table
3) were not available. It is noteworthy that 4% higher oil yield in plant
production could readily offset the additional cost associated with CO/steam
solubilization. Furthermore, there are other factors (like reaction kinetics)
which seem to favor CO/steam solubilization and which do not seem to be fully
accounted for in the feasibility studies.

Under the circumstances it is concluded that there is a need for further
verification of the effectiveness of the $CO/steam-K_2CO_3$ versus H_2 solubiliz-
ation. It is essential to carry out continuous two-stage coal/bitumen tests in
both ($CO/steam-K_2CO_3$ - H_2 versus H_2-H_2) modes in order to obtain more reliable
yield data and conversion values for economic analysis.

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Table 1

DEOXYGENATION OF THE FEEDSTOCK (COAL AND BITUMEN) AND
HYDROCARBON GAS YIELDS ON SOLUBILIZATION OF HIGHVALE COAL
IN BITUMEN USING CO/STEAM OR H_2 AT 390°C

	CO/Steam	H_2
Hydrocarbon Gas Yield (C_1-C_4)[a] (%)	1.0	0.9
Deoxygenation[b] (%)	86	94

a) on daf feedstock
b) defined as:
$$1 - \frac{\text{O in (distillable + extractable) products}}{\text{O in (coal + bitumen) feedstock}} \times 100\%$$

Table 2

THE EFFECT OF RESIDENCE TIME ON
CONVERSION FOR THE SOLUBILIZATION OF
HIGHVALE COAL IN BITUMEN WITH
CO/STEAM OR H_2 AT 390°C

Time (min)	Coal Conversion (on daf coal)	
	CO/Steam	H_2
0	58	10
15	65	34
30	85	65
60	86	68

Table 3

PRODUCT YIELDS AND COAL CONVERSIONS FROM THE
TWO-STAGE CO-PROCESSING OF BITUMEN AND HIGHVALE COAL

2nd Stage Catalyst	K_2MoO_4 - CH_3SSCH_3		
1st Stage Reducing Gas	H_2	CO/H_2O	$CO/H_2O-K_2CO_3$
Yield[a]			
Hydrocarbon Gas (C_1-C_5)	7.2($\pm$0.8)[b]	5.2($\pm$0.2)	5.3[c]
Distillable Oil (IBP-525°C)	62.3($\pm$0.9)	57.7($\pm$0.8)	66.2($\pm$0.7)
Soluble Extract	18.0($\pm$0.2)	19.3($\pm$0.9)	18.7($\pm$0.3)
Material Balance	94.1($\pm$3.1)	90.4($\pm$0.2)	96.1[c]
Coal Conversion (% daf coal)	90($\pm$1)	91($\pm$1)	98($\pm$0)

a) Yields are presented as % daf organic feed (bitumen + coal).
b) All data are quoted as the average values of two duplicate experiments.
   Figures in brackets show the spreads for the two experiments.
c) Single data point.

Table 4

OVERALL MASS BALANCE FOR THE OPTIMIZED ARC TWO-STAGE
$CO/H_2O-K_2CO_3$ - H_2 COAL/BITUMEN PROCESS

Bitumen Coal - 2.5/1
Basis 100 kg - feed (daf)

Component	Input	Output
C_5-200°C	3.1	11.0
200-375°C	15.0	40.1
375-525°C	16.1	19.0(2)
+ 525°C	37.2	12.3
Coal	28.6	
Ash	1.5(1)	
Unconverted Coal		2.7
Residue		1.84
Water	10.26	
H_2	0.6	
CO	26.1	
CO_2		44.7
H_2S		1.5
NH_4		0.46
C_1-C_4		5.2
Catalyst	0.34	
	138.8	138.8

(1) Ash reduced to 5% by deashing.
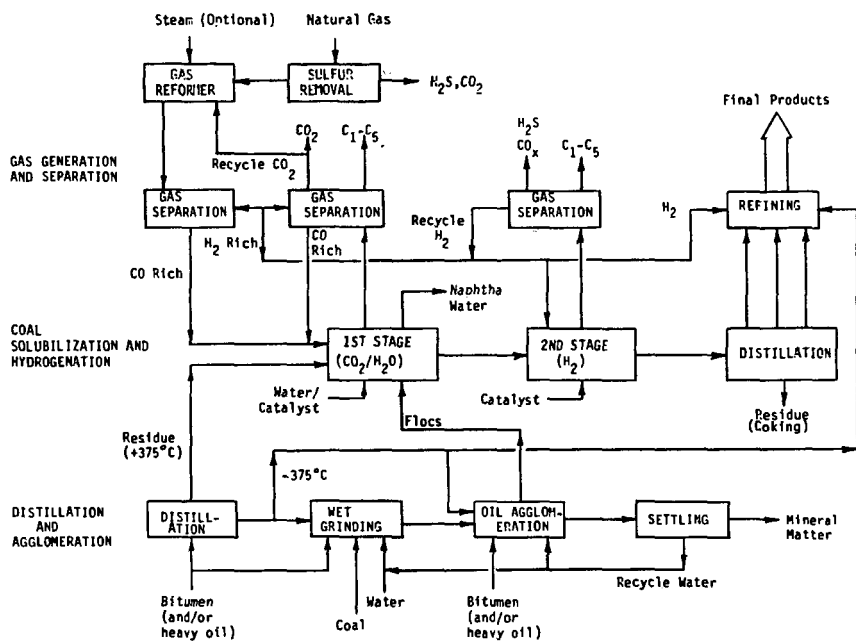(2) Estimate of yield after optimization.

Figure 1: Block Diagram of the ARC Two-Stage CO/Steam-K_2CO_3 - H_2
Coal/Bitumen Process Concept

COAL LIQUEFACTION/RESID HYDROCRACKING
VIA TWO-STAGE INTEGRATED CO-PROCESSING

Marvin Greene
Avinash Gupta
William Moon

LUMMUS CREST INC.
1515 BROAD STREET
BLOOMFIELD, NEW JERSEY 07003

BACKGROUND

Lummus Crest Inc. (LCI), a subsidiary of Combustion Engineering Inc., has been developing technology for the simultaneous processing of coal and heavy petroleum liquids under a joint development contract with the U. S. Department of Energy. The LCI co-processing route is an outgrowth of its Integrated Two-Stage Liquefaction (ITSL) technology developed over the past decade by LCI for coal liquefaction. A 33-month R&D contract was initiated in October 1984 with the objective of determining the technical and economic feasibility of coal liquefaction via the LCI co-processing route.

The project was formulated into five major program tasks as follows:

Task 1:	Project Management Plan
Task 2:	Feedstock Analysis
Task 3:	Co-Processing Reactivity Screening
Task 4:	Continuous Bench-Scale Operations
Task 5:	Cost Estimate of Conceptual Commercial Facility

The first three tasks have been completed and the continuous Bench-Scale Operations task has recently been initiated. The balance of this paper will describe experimental methods, the LCI co-processing approach and the results of recent bench-scale unit operations.

SOME JUSTIFICATIONS FOR CO-PROCESSING

Since co-processing inherently requires two separate feedstocks, namely coal and petroleum resid, it is possible to assess any potential process advantages from two viewpoints. From the refiner's viewpoint, the aromatic-rich, coal-derived extracts, being well known hydrogen donor solvents, can improve the hydroprocessing conversion of heavy, low grade petroleum feedstocks. On a constant energy cost basis, the syncrude cost contribution from a coal feedstock may be less than that from a petroleum feedstock.

For example, if one assumes a typical net syncrude yield of 0.0005 M^3/Kg (3.0 bbl/ton) for a run-of-mine bituminous coal priced at \$0.033/Kg (\$30/ton), then the coal feedstock cost of the coal syncrude is about \$62/M^3 (\$10.00/bbl). This compares to petroleum crude prices, even under the current suppressed spot market, in excess of \$74-100/M^3 (\$12-16/bbl). The situation is even more pronounced in the case of a typical subbituminous coal. Although the net yield of liquids from subbituminous coal is lower than that from bituminous coal (0.0003 M^3/Kg vs. 0.0005 M^3/Kg for bituminous), the corresponding subbituminous R.O.M. coal cost is not proportionately lower but rather about 73 percent lower than that of the bituminous coal (\$0.0088/Kg vs. \$0.033/Kg). This translates to a subbituminous coal feedstock cost of the coal liquids of about \$32.6/M^3 (\$5.20/bbl). In both cases, it is envisioned that a relatively low level of coal-derived liquids would be blended with petroleum resid feedstock so as not to greatly alter the downstream refinery processability of the petroleum-coal liquid mixtures.

From a coal liquefaction plant owner's viewpoint, the introduction of petroleum resid allows for a reduction in the large and costly solvent recycle systems. Additional advantages include:

o   Reduces net hydrogen consumption and correspondingly reduced hydrogen production costs;

o   Avoids the need for a costly deashing step;

o   Provides for a more rapid introduction of coal into the domestic energy networks; and

o   Allows the consideration of smaller-scale, less capital intensive plant sizes in an over-the-fence concept rather than in a grass-roots, mega-project concept.

LCI CO-PROCESSING APPROACH

Of the three key co-processing routes - thermal, thermocatalytic, biochemical - the LCI approach represents a hybrid of the first two in that it consists of a two-stage method. The first-stage is a thermal reaction system paralleling the Short Contact Time (SCT) reaction system developed for LCI's ITSL Process. The second-stage consists of a catalytic reaction system based on LCI's proprietary expanded-bed technology known as LC-Fining^{sm}. The SCT reactor is close-coupled to the LC-Fining^{sm} reactor to allow for rapid stabilization of coal extracts by the LC-Fining^{sm} catalyst thereby minimizing undesirable free radical condensation reactions.

Figures 1 and 2 show two alternative flowschemes depending upon the source and type of the petroleum resid. The scheme shown in Figure 1 is predicated on the use of a heavy refinery stream such as the unconverted resid from a catalytic hydrocracker. In this scheme, the petroleum feedstock is blended with the coal and a recycle gas oil stream prior to the first-stage, SCT thermal reactor.

The scheme shown in Figure 2 is predicated on the use of a virgin vacuum residua which is fed directly into the LC-Finer^{sm} along with the SCT coal extract. The first-stage reactor of the LC-Finer^{sm} can be operated to simultaneously optimize the production of a) a donor solvent-rich gas oil recycle stream; b) an unconverted but hydrotreated recycle resid stream having improved solvency for coal; and c) hydrocracked C_5-524°C (C_5-975°F) distillates.

EXPERIMENTAL APPROACH

The experimental approach to obtaining key process data required for the preliminary design and estimate of a conceptual commercial facility has been accomplished in a variety of test units. Initial work for screening candidate coal and petroleum feedstocks was carried out in microautoclave reaction systems shown schematically in Figure 3. This was followed by testing in a continuous, close-coupled test unit under once-through conditions utilizing solvents characteristic in composition to what is expected at steady-state, but synthetically generated. The test unit, shown schematically in Figure 4, consists of an SCT reaction system comprised of a 6.2 mm i.d. by 343 cm long horizontal coil heater followed by a vertical SCT reactor having a volume of 118 cc. The SCT

(sm) LC-Fining is a service mark of Lummus Crest Inc. for engineering, marketing and technical services related to hydrocracking and hydrodesulfurization processes for reduced crude and residual oils.

system, which could be operated with either SCT reactors described above, was close-coupled to a stirred autoclave catalytic hydrocracker. The continuous bench-scale unit being operated in Task 4 consists of the above SCT reactor systems close-coupled to a small diameter, expanded-bed LC-Fining^{sm} reactor system. This unit can operate in a recycle mode which consists of batch collection of hydrotreated liquids from the LC-Finer^{sm} followed by batch slurrying of the coal and the thus collected recycle liquids. Both SCT and LC-Finer^{sm} reactors are operated continuously.

RESULTS OF BENCH-SCALE TESTING

Process variables studies, carried out in the continuous close-coupled test units, have recently been completed. The bulk of the test scans concentrated on scouting of both SCT and LC-Fining^{sm} reaction conditions close to that of the anticipated region of preferred commercial operations. Tests were made with two coal-petroleum combinations that were selected from the analysis of the microautoclave test data. These combinations consisted of a bituminous coal - Pittsburgh seam with Athabasca vacuum resid - and a subbituminous coal - Wyodak with Arab Heavy vacuum resid. During the scans, two sets of data were obtained indicating the effect of LC-Fining^{sm} reactor temperature and solvent/coal ratio on co-processing performance.

EFFECT OF TEMPERATURE

The impact of LC-Fining^{sm} temperature at constant SCT reaction conditions is shown in Table 1. From these data, we have calculated pseudo-kinetic rate constants for each of the performance criteria based on simplified kinetic models. These values are indicated below:

Co-Processing (SCT & LC-F) Performance Parameter	Pseudo-Rate Constant, hr^{-1}		
	404C	416C	432C
Desulfurization	0.75	1.09	1.67
Demetallization	0.55	0.90	1.12
524C+ Conversion	0.54	0.72	1.11
Denitrogenation	0.29	0.43	0.90

The feedstock in all tests consisted of 25 percent coal/37.5 percent hydrotreated petroleum resid/37.5 percent coal-derived gas oil. The order of reactivity as measured by the specific co-processing performance parameters in descending order is:

Desulfurization > Demetallization > Conversion > Denitrogenation

It is also interesting to note that in all three tests, the preasphaltene content in the product of the single-stage LC-Finer^{sm} has been reduced to less than 2 percent.

EFFECT OF SOLVENT QUALITY AND SOLVENT/COAL RATIO

The impact of solvent/coal ratio and solvent quality at constant SCT and LC-Fining^{sm} reaction conditions is shown in Table 2. The following interesting observations have been made based on the data shown:

    o   At constant coal slurry concentration, reducing the ratio of the solvent (524^{0}C- boiling range) to coal from 1.5/1 to 1.0/1 had a minimal effect on observed coal conversions.

o   However, the reduction in the said solvent/coal ratio did adversely affect syncrude characteristics and net distillate yields.

It should be kept in mind that the high LC-Fining^{sm} severity used in this particular test campaign was aimed at assessing per pass performance (e.g., conversion, desulfurization, etc.) limits during co-processing. In the conceptual commercial concept depicted in Figures 1 and 2, it is anticipated that the first-stage LC-Finer^{sm} located immediately downstream of the SCT reactor will be operated under optimal conditions for generating recycle gas oil solvents having high hydrogen donor capacity. At these severities, it is anticipated that the $524^{o}C+$ conversions would be lower than the values shown in Table 4. The additional required feed conversions, i.e., overall conversions in excess of 80 percent, could be achieved in a second-stage LC-Finer^{sm} operated at higher, more conventional petroleum hydrocracking severities.

In test BSCL-20, a $524^{o}C-$ recycle solvent during co-processing was simulated by blending a neat coal-derived hydrogenated solvent with a neat petroleum-derived hydrogenated solvent in the same ratio as that of the coal and petroleum resid fed in that run. By comparing these results to those of test BSCL-9 made only with coal-derived $524^{o}C-$ solvent, it is possible to estimate the relative solvent quality index (SQI) of the petroleum-derived gas oil solvent in comparison to that of the coal-derived gas oil solvent. The SQI of the particular petroleum gas oil utilized in this test has been estimated to be about 60 percent of that of the coal-derived solvent based on relative solvent performance as measured by observed net distillate yields. Optimization of the petroleum resid hydrocracking step in which the simulated gas oil solvent was generated has the potential to increase the latter's SQI value closer to that of the coal-based solvent.

FUTURE WORK

The continuous bench-scale unit will be operated in the recycle mode to demonstrate the effect of solvent maintenance on co-processing performance as a function of feedstock types (Pittsburgh seam and Wyodak coals; Arab Heavy and Athabasca residua); coal/resid ratios; solvent/coal ratio and catalyst age. These data will serve as the basis for formulating a conceptual commercial plant design. Towards the end of the Task 4 experimental program, a catalyst life test at preferred co-processing conditions will be made to demonstrate the technical feasibility of the base case design.

ACKNOWLEDGEMENTS

TABLE 1

EFFECT OF LC-FINING[SM] TEMPERATURE ON CLOSE-COUPLED CO-PROCESSING PERFORMANCE

SUMMARY OF TEST CONDITIONS AND RESULTS

Run No. (BSCL-)	9	10	11
I. Test Conditions			
SCT Temperature, ^{o}C (^{o}F)	449(840)	449(840)	449(840)
LC-Fining[SM] Temperature, ^{o}C (^{o}F)	432(810)	416(780)	404(760)
Coal Space Velocity to SCT, Kg/Hr/M^3	3400	3400	3400
Solvent/Coal Wt. Ratio	1.5	1.5	1.5
Resid/Coal Wt. Ratio	1.5	1.5	1.5
II. Test Results			
Coal Conversion, Wt.% MAF	96.0	93.8	93.7
524^{o}C+ (975F+) Conversion, Wt.%	75.8	67.3	58.4
Net Distillate Yield, Kg 524^{o}C-/100 Kg 524^{o}C+	58.1	55.9	48.3
Desulfurization, %	82.5	75.7	66.0
Denitrogenation, %	71.7	55.0	43.0
Resid Demetallization, %	76.0	72.0	59.0
Preasphaltenes Concentration, %	1.7	1.5	1.9

(1) Feedstocks: Pittsburgh seam coal; Prehydrotreated 524^{o}C+ Athabasca resid

(2) Solvent: 524^{o}C- gas oil characteristic of a coal-derived recycle solvent produced in LCI's ITSL PDU during Wyodak coal operations

(3) SCT Condition: 137 atm; 360 M^3 H$_2$/M^3 feed

(4) LC-Fining[SM] Conditions: Shell 324M catalyst; 137 atm; 0.4R hr^{-1}; 530 M^3 H$_2$/M^3 feed

TABLE 2

EFFECT OF SOLVENT QUALITY AND SOLVENT/COAL RATIO ON CLOSE-COUPLED CO-PROCESSING PERFORMANCE

SUMMARY OF TEST CONDITIONS AND RESULTS

Run No. (BSCL-)	9	21	20
I. Test Conditions			
Solvent/Coal Wt. Ratio	1.5	1.0	1.5
Coal/Resid Wt. Ratio	0.67	0.50	0.67
Coal Slurry Concentration, Wt.%	25.0	25.0	25.0
$524^{O}C-$ Solvent Composition, Wt.%			
ITSL*	100	100	40
Petroleum Gas Oil**	0	0	60
SCT Temperature, ^{O}C (^{O}F)	449(840)	449(840)	449(840)
LC-Fining^{SM} Temperature, ^{O}C (^{O}F)	432(810)	432(810)	432(810)
Coal Space Velocity to SCT, Kg/Hr/M^{3}	3400	3400	3400
II. Test Results			
Coal Conversion, Wt.% MAF	96.0	93.4	94.2
$524^{O}C+$ (975F+) Conversion, Wt.%	75.8	66.2	64.2
Net Distillate Yield, Kg $524^{O}C-$/100 Kg $524^{O}C+$	58.1	51.0	46.0
Desulfurization, %	82.5	75.0	77.2
Denitrogenation, %	71.7	65.0	67.1
Resid Demetallization, %	76.0	69.0	71.0
Preasphaltenes Concentration, %	1.7	2.2	2.0

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* $524^{O}C-$ gas oil characteristic of a coal-derived recycle solvent produced in LCI's ITSL PDU during Wyodak coal operations.

** $524^{O}C-$ gas oil characteristic of a petroleum-derived recycle solvent produced during LC-Fining^{SM} of virgin Athabasca bitumen.

1. Feedstocks: Pittsburgh seam coal; prehydrotreated $524^{O}C+$ Athabasca resid

2. SCT Conditions: 137 atm; 360 M^{3} H$_{2}$/M^{3} feed

3. LC-Fining^{SM} Conditions: Shell 324M catalyst; 137 atm; 0.4R Hr^{-1}; 530 M^{3} H$_{2}$/M^{3} feed

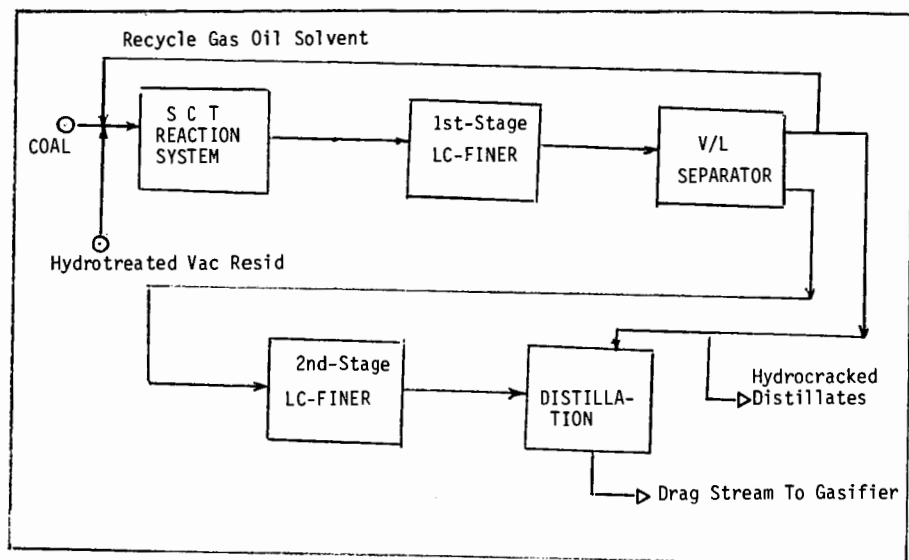Figure 1. SCHEMATIC OF LCI CO-PROCESSING CONCEPT WITH HYDROCRACKED PETROLEUM RESIDUA

Figure 2. SCHEMATIC OF LCI CO-PROCESSING CONCEPT WITH VIRGIN PETROLEUM RESIDUA
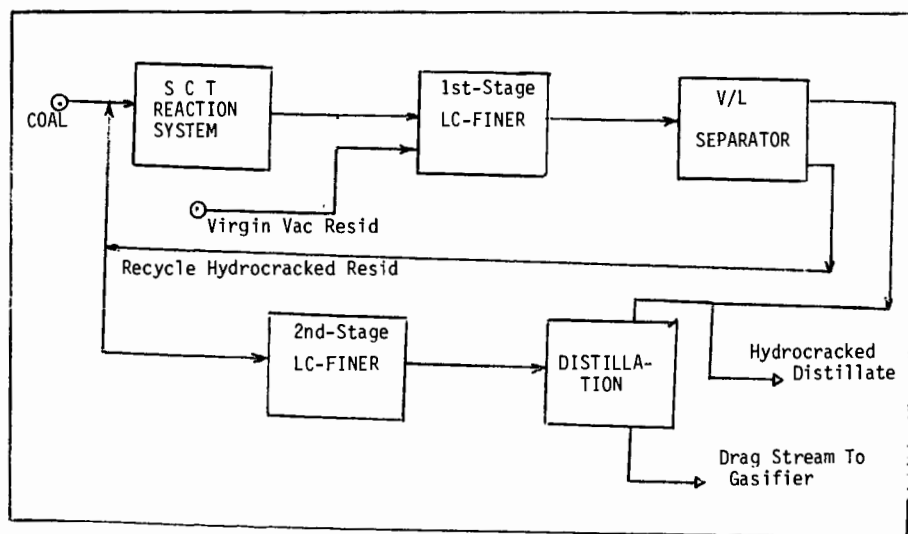
FIGURE 3
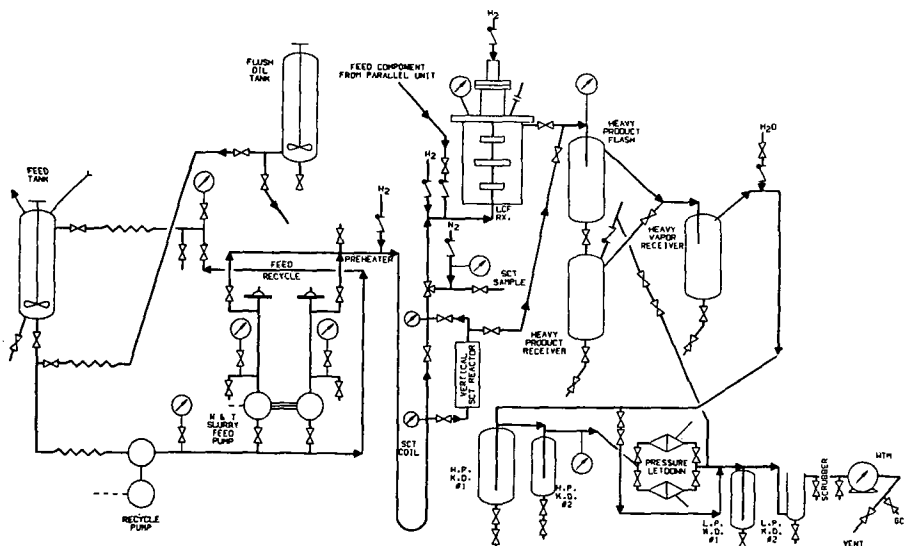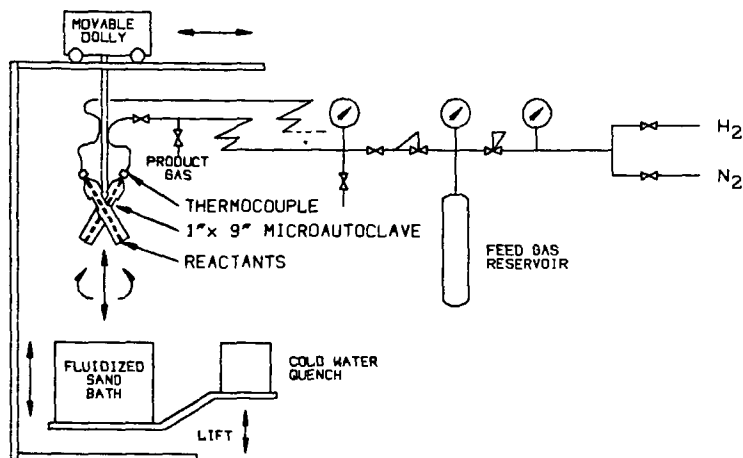## SCHEMATIC OF MICROAUTOCLAVE TEST UNIT

FIGURE 4   SCHEMATIC OF LCI'S CONTINUOUS CO-PROCESSING TEST UNIT

SIMULATION OF A COAL/PETROLEUM RESID COPROCESSING PILOT PLANT SCHEME

George W. Pukanic, Dennis N. Smith, and John A. Ruether

U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania 15236

ABSTRACT

Coprocessing involves the conversion of coal and heavy oil in the presence of hydrogen to products that can be further upgraded into commercial fuels; the upgrading can be carried out in an existing refining operation. This relatively new concept eliminates or significantly reduces the need for expensive solvent recycle, and thus has the potential for improved economic performance over current direct coal liquefaction processes.

A simulation of a single-stage coprocessing pilot plant involving the simultaneous conversion of resid and coal has been carried out using the ASPEN PLUS simulator. Limited experimental data were available for only one run, and results should be considered preliminary. The Assay Data Analysis and Pseudocomponent Correlation System of ASPEN PLUS has been used to develop a set of pseudocomponents for coal/ resid liquids and to estimate corresponding physical and thermodynamic properties. Correlations based on coal liquids and petroleum liquids have been utilized. For some process equipment, petroleum liquids correlations are better than coal liquids correlations. Testing for the presence of a free water phase and the treatment of heavy resid as a single high-boiling pseudocomponent has improved simulator performance.

INTRODUCTION

Serious research efforts are under way to develop alternative energy sources in order to prevent petroleum supply disruptions from having adverse impact upon the economy of those countries dependent on external supplies of petroleum. During the last twenty years, considerable work has been done in attempts to understand the scientific and technological applications of coal conversion schemes for production of liquid fuels to supplement dwindling petroleum reserves. A relatively new concept addressing this issue involves coprocessing heavy oil with relatively low-cost coals to produce a liquid distillates. A review of coal-oil coprocessing technology has been given by Cugini [1]. This review addresses the state of the technology, and several important research efforts required to advance the technology beyond the current level of knowledge. One important area of research required to improve understanding of coprocessing technology is the characterization of the heavy nondistillable feedstock and product oils. Estimations of physical and thermodynamic properties of feedstock and product oils are required to design the commercial reactor and the product separation train and to estimate material flows and compositions for internal and external streams of the coprocessing plant.

There are several sources of information related to coprocessing of coal and heavy oil in bench-scale and pilot-plant operations [2-4]. However, insufficient information is given in these reports to properly characterize the thermodynamic and physical properties of the liquid products as a function of operating conditions. Coal and heavy oil coprocessing in a continuous bench-scale plant has recently been initiated at UOP, Inc. and the Signal Research Center, Inc. [5]. The work related to this study has been described in sufficient detail to allow characterization of the products. The present effort describes the results of a simulation of the single-stage coprocessing bench-scale unit at Signal Research Center, Inc., using the ASPEN PLUS simulator to determine physical and thermodynamic properties

of the liquid products. This bench-scale work forms a preliminary basis to conduct process modeling studies for a range of operating conditions used with this concept.

EXPERIMENTAL

The simulation studies were based on one catalytic coprocessing run at the UOP pilot plant (Figure 1). Two parts of Lloydminster resid to one part of Illinois No. 6 coal constituted the feed. The Lloydminster resid was fractionated so that 95% of the resid consisted of $950^\circ F+$ material. Total feed rate to the reactor was 3.75 lb in 12 hours. Coal conversion defined as toluene insolubles was 86%. Operating conditions for the separators include the following: high-pressure separator--temperature = $302^\circ F$, pressure = 3114.7 psia; three-phase separator--temperature = $86^\circ F$, pressure = 3014.7 psia; low-pressure separator--temperature = $284^\circ F$, pressure = 19.7 psia; debutanizer--temperature = $43^\circ F$, pressure = 17.7 psia; vacuum fractionator--temperature = $608^\circ F$, pressure = 0.94 psia. The effluent from the low-pressure separator and gases from the vacuum pump are sent to the debutanizer, where C_6+ material is condensed and off-gases are sampled. The vacuum fractionator is a packed column that operates with an overhead reflux. Dimensions of the debutanizer and vacuum fractionator towers and of their packing were not available. For lack of better information on the number of equivalent theoretical plates in the debutanizer and vacuum fractionator, simulations for both units were performed as simple flash calculations.

Experimental values were available for the three-phase separator vapor stream, the debutanizer vapor stream, the vacuum fractionator bottoms, and a combined composition for the vacuum fractionator overhead and debutanizer bottoms. Gas phase components were analyzed by gas chromatography. Boiling point distributions were obtained by gas chromatographic simulated distillation.

FLOWSHEET SIMULATION METHODOLOGY

The ASPEN PLUS simulator [6] has been used for the flowsheet analysis of the separator system downstream from the reactor in the UOP coprocessing pilot plant (Figure 1). ASPEN PLUS was originally designed for the analysis of fossil fuel conversion processes, although it has proven useful for many process industries. It has been used to develop a reference data base system of thermophysical properties of coal liquids needed for vapor-liquid equilibrium and for heat and material balance calculations [2], and to simulate the preliminary separator system downstream from the reactor in the SRC-II coal liquefaction process [7].

A preliminary step in the simulation process is the development of an ASPEN flow-sheet. Figure 2 represents the ASPEN flowsheet for the separator system following the reactor in the coprocessing pilot-plant flow diagram in Figure 1. The outlet stream from the reactor is the process feed stream for the simulation. The five separators include a high-pressure separator, a three-phase separator, a low-pressure separator, a debutanizer, and a vacuum fractionator. All are modeled as flash units where vapor-liquid equilibrium calculations are performed to produce vapor and liquid outlet streams. Mixer units are used to combine material streams into one stream. Names associated with the streams, and unit operation models for ASPEN identification purposes are designated in Figure 2.

Thermophysical properties used for the simulations were based on three ASPEN PLUS option sets. The option set used for lighter components up to C_6 is based primarily on the Redlich-Kwong-Soave thermophysical model. Heavier components were analyzed using the ASPEN PLUS Assay Data Analysis and Pseudocomponent Correlation System for petroleum liquids and coal liquids. Standard API procedures were used for the petroleum liquids thermophysical models, and correlations developed primarily at Aspen Technology, Inc., were used for the coal liquids thermophysical models. From assay analyses of the vacuum fractionator process streams, a set of

20 pseudocomponents was developed to represent the heavier components; each pseudocomponent represents about a 50°F cut of liquid distillate. Since the process feed stream included both coal and petroleum liquids, separate simulation runs were made where thermophysical properties for each pseudocomponent were analyzed using the correlation option set for coal liquids and the set for petroleum liquids. Comparisons have been made for the performance of each option set.

RESULTS AND DISCUSSION

The composition for the process feed stream to the high-pressure separator is estimated from experimental product slates for the vacuum fractionator, the debutanizer, and the three-phase separator (see Table 1). Gases and identified compounds range from H_2 to pentane. Liquid distillates are represented as pseudocomponents and range from an average boiling point of 111°F to 1091°F (pseudocomponents are prefaced by PC and followed by the average boiling point of the approximately 50°F cut). The initial boiling point (IBP) of the liquid distillate is 69.8°F. For conciseness in the presentation of results, the pseudocomponents have been expressed as four distillate fractions (see Table 2).

TABLE 1. Process Feed Stream Composition for High Pressure Separator

Components*	Flows (lb/hr)	Components*	Flows (lb/hr)
H_2	0.0593	PC428	0.0075
CO	0.0051	PC477	0.0168
H_2S	0.0552	PC525	0.0163
CH_4	0.0637	PC575	0.0163
C_2H_6	0.0364	PC625	0.0167
C_3H_8	0.0255	PC675	0.0174
C_4H_{10}	0.0105	PC725	0.0158
$I-C_4H_{10}$	0.0028	PC774	0.0139
C_5H_{12}	0.0034	PC825	0.0128
$I-C_5H_{12}$	0.0034	PC876	0.0113
H_2O	0.0108	PC924	0.0113
PC111	0.0052	PC973	0.0048
PC176	0.0017	PC1022	0.0034
PC226	0.0020	PC1091	0.0503
PC276	0.0025	Ash	0.0108
PC327	0.0041	Unconverted Coal	0.0135
PC376	0.0053	Nondistillate Solids	0.0456

*Pseudocomponents are 50°F cuts and are represented by PC followed by the average boiling point.

TABLE 2. Process Feed Stream Distillate Fractions Expressed as Pseudocomponents.

Distillate Fraction	Pseudocomponent Range	Flows (lb/hr)
IBP-350°F	PC111-PC327	0.0155
350°-450°F	PC376-PC428	0.0128
450°-950°F	PC477-PC924	0.149
950°F+	PC973-PC1091	0.0585

Three-Phase Separator
For the three-phase separator overheads, the effect of the correlation option is given in Table 3. There is some improvement using the petroleum-liquids option set. Use of the coal-liquids option set results in an overall error for total mass flow of overhead of 1.86%, and the petroleum-liquids option set results in an error of 0.73%.

TABLE 3. Comparison of Calculated and Experimental Overhead Flows (lb/hr) for the Three-Phase Separator as a Function of Physical Properties Calculations Method

	Correlation Option Set		
Components	Coal Liquids	Petroleum Liquids	Experimental
H_2	0.0591	0.0589	0.0587
CO	0.0051	0.0051	0.00513
H_2S	0.0516	0.0511	0.0498
CH_4	0.0629	0.0626	0.0621
C_2H_6	0.0349	0.0346	0.0340
C_3H_8	0.0233	0.0229	0.0225
C_4H_{10}	0.0086	0.0084	0.00849
$I-C_4H_{10}$	0.0024	0.0023	0.00212
C_5H_{12}	0.0023	0.0022	0.00263
$I-C_5H_{12}$	0.0025	0.0023	0.00263

Debutanizer
For the debutanizer overheads, the effect of the correlation option is given in Table 4. There is improvement using the petroleum-liquids option set. Use of the coal-liquids option set results in an overall error for total mass flow of overhead of 16.4%, and the petroleum-liquids option set results in an error of only 1.37%.

TABLE 4. Comparison of Calculated and Experimental Overhead Flows (lb/hr) for the Debutanizer as a Function of Physical Properties Calculations Method

	Correlations Options Set		
Components	Coal Liquids	Petroleum Liquids	Experimental
H_2	2.31×10^{-4}	3.91×10^{-4}	6.09×10^{-4}
CO	2.79×10^{-5}	4.59×10^{-5}	--
H_2S	3.5×10^{-3}	3.9×10^{-3}	--
CH_4	7.84×10^{-4}	1.1×10^{-3}	1.60×10^{-3}
C_2H_6	1.4×10^{-3}	1.8×10^{-3}	2.35×10^{-3}
C_3H_8	2.1×10^{-3}	2.5×10^{-3}	2.96×10^{-3}
C_4H_{10}	1.5×10^{-3}	1.8×10^{-3}	1.95×10^{-3}
$I-C_4H_{10}$	3.34×10^{-4}	4.02×10^{-4}	6.51×10^{-4}
C_5H_{12}	6.15×10^{-4}	7.41×10^{-4}	8.08×10^{-4}
$I-C_5H_{12}$	6.10×10^{-4}	7.31×10^{-4}	8.08×10^{-4}
C_6^+	1.05×10^{-3}	1.35×10^{-3}	2.88×10^{-3}

Vacuum Fractionator
As a measure of simulation adequacy, total vapor and liquid flows computed by simulation were compared with experimental data. Total mass flow of overhead and

bottoms is less sensitive to the number of theoretical stages than are the individual distillate fraction flows. The effect of the correlation option set (coal-liquids vs. petroleum-liquids) on the vacuum fractionator simulation performance was determined. Since simulated distillate flows were in considerable disagreement with experimental values for the reported operating pressure of 0.94 psia, additional simulation runs were made to observe the effect of assumed column pressures. For the petroleum-liquids option set, a value of 4.5 psia gave the best match of calculated total overhead and bottom flows to experimental flows. Correspondingly, a value of 6.0 psia was found for the coal-liquids option set. Given that the reported column pressure, 0.94 psia, is closer to 4.5 psia than to 6.0 psia, this result gives an indirect indication that the petroleum-based option set better describes the experimental system. The actual operating pressure for the vacuum fractionator was known to increase above 0.94 psia during the experimental run, but no information is available as to the extent of increase. The results for the flows of the distillate fractions are presented in Tables 5-7. Table 5 represents results for vacuum bottoms flows, and Table 6, for vacuum overhead flows (calculated vacuum overhead flows also include values for debutanizer bottoms flows in order to agree with experimental measurements). Table 7 gives a comparison of the pressure and correlation option set in terms of an overall percentage error for both bottoms and overhead at the operating pressure of 0.94 psia. Use of the petroleum-liquids option set gives better agreement, although the percentage of error relative to experimental error is still considerable.

TABLE 5. Comparison of Calculated and Experimental Vacuum Bottoms Flows (lb/hr) as a Function of Physical Properties Calculation Method and System Pressure

Correlation Option Set	Boiling Point Range, °F	Calculated	Experimental
Coal Liquids			
P = 0.94 psia	IBP-350	1.52×10^{-6}	--
	350-450	8.46×10^{-5}	--
	450-950	5.60×10^{-3}	5.16×10^{-2}
	950+	3.24×10^{-2}	5.92×10^{-2}
	Total	3.80×10^{-2}	1.11×10^{-1}
P = 6.0 psia	IBP-350	5.38×10^{-5}	--
	350-450	2.94×10^{-4}	--
	450-950	5.47×10^{-2}	5.16×10^{-2}
	950+	5.67×10^{-2}	5.92×10^{-2}
	Total	1.12×10^{-1}	1.11×10^{-1}
Petroleum Liquids			
P = 0.94 psia	IBP-350	4.92×10^{-6}	--
	350-450	2.47×10^{-5}	--
	450-950	1.40×10^{-2}	5.16×10^{-2}
	950+	5.38×10^{-2}	5.92×10^{-2}
	Total	6.78×10^{-2}	1.11×10^{-1}
P = 4.5 psia	IBP-350	5.59×10^{-5}	--
	350-450	2.75×10^{-4}	--
	450-950	5.21×10^{-2}	5.16×10^{-2}
	950+	5.79×10^{-2}	5.92×10^{-2}
	Total	1.10×10^{-1}	1.11×10^{-1}

TABLE 6. Comparison of Calculated and Experimental Vacuum Overhead Flows (lb/hr) as a Function of Physical Properties Calculation Method and System Pressure

Correlation Option Set	Boiling Point Range, °F	Calculated	Experimental
Coal Liquids			
P = 0.94 psia	IBP-350	1.07×10^{-2}	1.34×10^{-2}
	350-450	1.28×10^{-2}	1.90×10^{-2}
	450-950	1.43×10^{-1}	8.97×10^{-2}
	950+	2.60×10^{-2}	8.17×10^{-5}
	Total	1.93×10^{-1}	1.22×10^{-1}
P = 6.0 psia	IBP-350	1.07×10^{-2}	1.34×10^{-2}
	350-450	1.25×10^{-2}	1.90×10^{-2}
	450-950	9.38×10^{-2}	8.97×10^{-2}
	950+	1.70×10^{-3}	8.17×10^{-5}
	Total	1.19×10^{-1}	1.22×10^{-1}
Petroleum Liquids			
P = 0.94 psia	IBP-350	1.05×10^{-2}	1.34×10^{-2}
	350-450	1.28×10^{-2}	1.90×10^{-2}
	450-950	1.34×10^{-1}	8.97×10^{-2}
	950+	4.60×10^{-3}	8.17×10^{-5}
	Total	1.62×10^{-1}	1.22×10^{-1}
P = 4.5 psia	IBP-350	1.05×10^{-2}	1.34×10^{-2}
	350-450	1.25×10^{-2}	1.90×10^{-2}
	450-950	9.64×10^{-2}	8.97×10^{-2}
	950+	5.08×10^{-3}	8.17×10^{-5}
	Total	1.24×10^{-1}	1.22×10^{-1}

TABLE 7. Comparison of Physical Properties Calculation Method on Vacuum Fractionator Effluent Stream Mass Flow Rates

Correlation Option Set	% Error*	
	Vacuum Bottoms	Vacuum Overhead
Coal Liquids		
P = 0.94 psia	65.8	58.2
Petroleum Liquids		
P = 0.94	38.9	32.8

*Absolute value of (Calculated - Experimental)/Experimental.

Effects of pressure and correlation option set on pseudocomponent composition for the vacuum fractionator are reflected in Figures 3-6. Figures 3 and 4 represent the effect on the vacuum bottoms stream, and Figures 5 and 6, the effect on the overhead stream. These figures indicate that the petroleum-liquids option set gives better values than the coal-liquids option set and that the effect of pressure is considerable.

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Low Pressure Separator

A temperature of 284°F was used for the operating condition of the low-pressure separator in the simulator. Since, experimentally, a temperature range of 248°F-284°F was given, it was decided to make a simulation run at the lower temperature to determine any effects of the assumed temperature on the effluent flow rates. Results for the lower temperature indicate only a small increase in bottoms flows of 1.3% and an decrease in overhead flows of 11.8%.

Effect of Free Water Phase on the Debutanizer

Simulations were carried out on the debutanizer to determine the impact of the presence of a free water phase (Table 8). Without the invocation of the option to test for the presence of free water, no distillate and only a small amount of lighter gases are predicted by the simulator to be present in the debutanizer bottoms. With the test for the presence of water invoked, the presence of a free water phase is confirmed, and results indicate a substantial increase in bottoms flow and a decrease in overhead. Both of these predictions agree with experiment, as shown in Table 8. All simulations have tested for the presence of a free water phase.

TABLE 8. Effect of Treatment of Water on the Debutanizer Effluent Product Flows (lb/hr)

Products	Assumed Absence of Free Water Phase		Assumed Presence of Free Water Phase		Experimental Overhead
	Overhead	Bottoms	Overhead	Bottoms	
Gases-C_5	6.93×10^{-3}	3.90×10^{-6}	1.11×10^{-2}	1.16×10^{-3}	1.18×10^{-2}
IBP-350°F	3.79×10^{-3}	0	1.05×10^{-3}	4.86×10^{-3}	
350°-450°F	1.53×10^{-3}	0	1.08×10^{-7}	1.16×10^{-3}	
450°-950°F	1.31×10^{-3}	0	4.69×10^{-8}	8.46×10^{-4}	2.88×10^{-3}
950°F+	1.02×10^{-7}	0	0	6.52×10^{-8}	

TABLE 9. Effect of Treatment of Heavy Resid on Vacuum Bottoms

Product	Heavy Residue Treated as	
	Solid Material (Flows, lb/hr)	Pseudocomponent (Flows, lb/hr)
Gases-C_5	0	1.44×10^{-8}
IBP-350°F	0	1.52×10^{-6}
350°-450°F	0	8.47×10^{-6}
450°-950°F	0	5.59×10^{-3}
950°F+	0	3.25×10^{-2}
Nondistillate Solid	0.0456	0

Effect of Treatment of Heavy Resid on Vacuum Bottoms

The method of treatment of heavy resid has an impact on predicted composition and flow rate of vacuum bottoms as reflected in Table 9. The data are for the simulation of the vacuum fractionator at the pressure of 0.94 psia and using coal-liquids correlations. When the heavy resid is treated as a nondistillate solid, i.e., material with negligible vapor pressure, no distillates are predicted to appear in the vacuum bottoms. When the heavy resid is treated as a 1091°F pseudo-

component, distillate products are predicted in the bottoms. This treatment of
the resid fraction corresponds to that of McKeegan and Klunder [8], who also
assigned a single normal boiling point to the nondistillate material in their
simulation of the separator system in the SRC-II coal liquefaction process
(although they used a much higher temperature). The plot in Figure 4 for P = 0.94
psia, as well as for P = 6.0 psia, reflects the presence of heavy resid treated as
the 1091°F pseudocomponent. These plots are in line with the experimental obser-
vation of the presence of significant amounts of liquid distillate product in the
vacuum bottoms stream. All simulation results for the vacuum fractionator pre-
sented in Tables 5-7 and Figures 3-6 have treated the heavy resid as a 1091°F
pseudocomponent.

CONCLUSIONS

The very preliminary results reported here indicate that the use of petroleum-
liquids correlations may result in an improvement over coal-liquids correlations
in the simulation of the coprocessing of Lloydminster with Illinois No. 6 coal.
Agreement between simulation and experiment is improved by using a higher assumed
pressure than the experimental pressure for the vacuum fractionator, by treating
the presence of water as a free water phase, and by treating the heavy resid as
1091°F distillate rather than an inert solid material. It is necessary to obtain
better definition of the separation equipment used and the operating conditions
employed, and to acquire a larger data set in order to evaluate the present
capability for simulating the separation steps in coprocessing.

ACKNOWLEDGMENT

DISCLAIMER

Reference in this report to any specific product, process, or service is to
facilitate understanding and does not necessarily imply its endorsement or favor-
ing by the United States Department of Energy.

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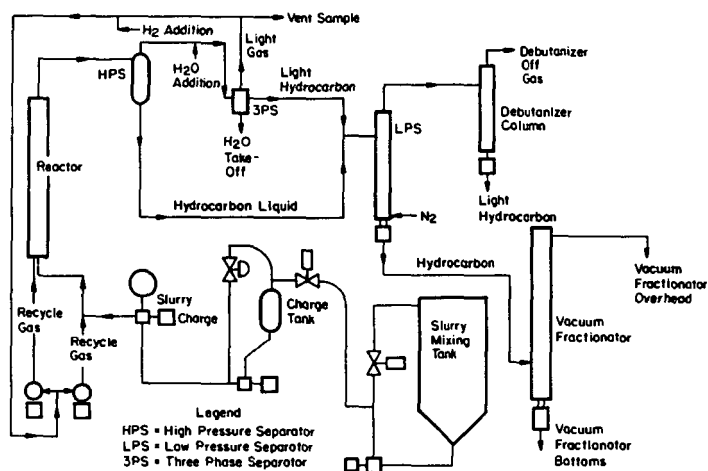
Figure 1 - UOP Coprocessing Pilot-plant Flow Diagram.
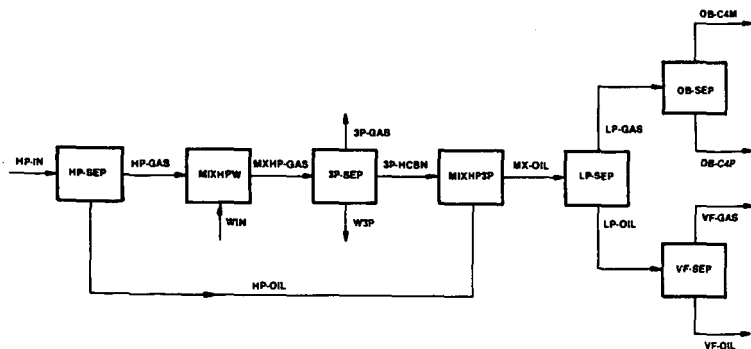
FIGURE 2. ASPEN FLOWSHEET OF SEPARATOR SYSTEM FOR UOP COPROCESSING PILOT-PLANT FLOW SCHEME.
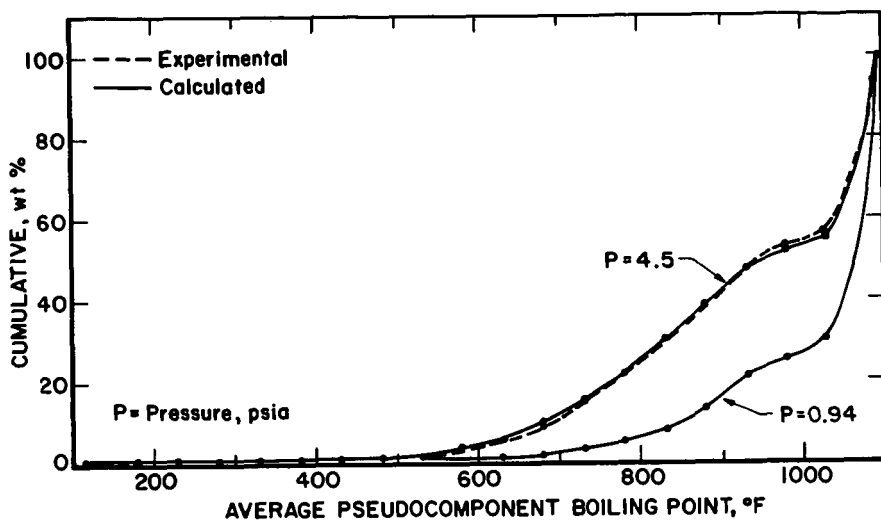
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Figure 3 - Composition of Vacuum Bottoms Pseudocomponents Using Petroleum Liquids Correlations.
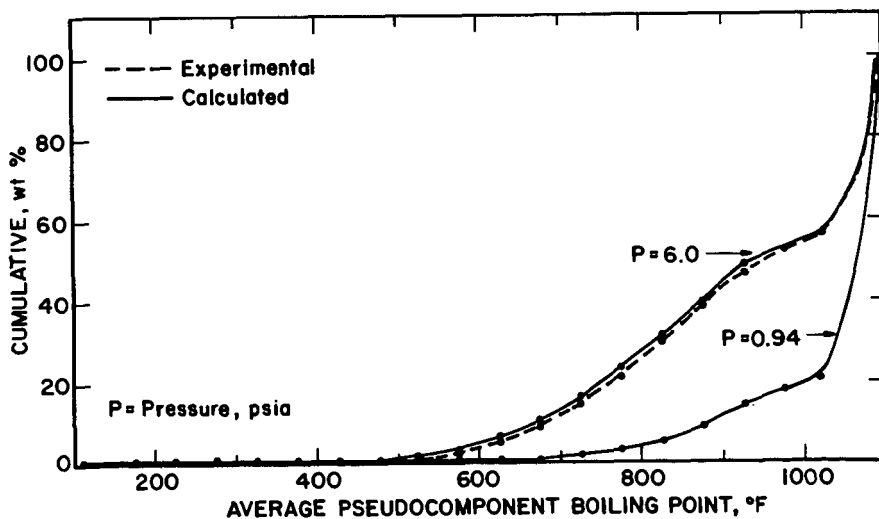

Figure 4 - Composition of Vacuum Bottoms Pseudocomponents Using Coal Liquids Correlations.
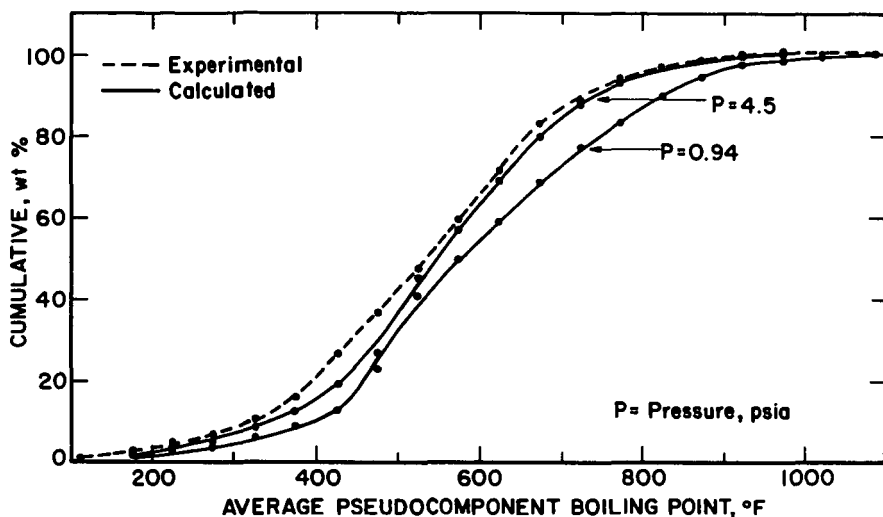
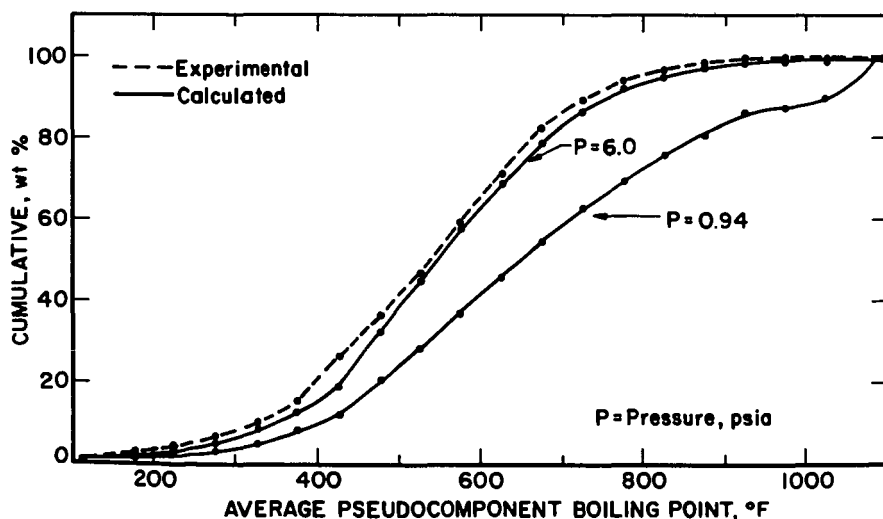Figure 5 - Composition of Vacuum Overhead Using Petroleum Liquids Correlations.

Figure 6-Composition of Vacuum Overhead Using Coal Liquids Correlations.

AN ASSESSMENT OF THE POTENTIAL FOR COAL/RESIDUAL OIL COPROCESSING

D.A. Huber, Q. Lee and R.L. Thomas   K. Frye and G. Rudins

Burns and Roe   U.S. DOE
Oradell, NJ   Germantown, MD
07649   20585

Abstract

Among the promising new techniques to produce liquid hydrocarbon fuels from coal is coal/petroleum coprocessing based upon the use of heavy oil, tar sand bitumen and petroleum residua as "solvents" for the conversion of coal. Coprocessing is the simultaneous hydrogenation of coal and heavy oil fractions in specially designed reactors with coal contents by weight ranging from as low as 1% to potentially as high as 50-60% depending upon the technology employed. The results of a study on the potential for coal/residual oil coprocessing in the United States are addressed in this paper.

Introduction

Economics, the desire for less dependence upon the importation of foreign oil, and the depletion of lighter crudes in the United States has led the refining industry to process heavier crudes and bitumens. Upgrading and converting these heavy oils to distillate liquids using conventional petroleum thermal cracking, catalytic cracking and/or hydrocracking technologies has required the installation of costly equipment to handle the heavier oils. There exists in the literature sufficient evidence to suggest that heavy oil converts more readily in the presence of coal and that significant demetallization, desulfurization, denitrification and conversion of asphaltenes to oils also occurs. Thus the simultaneous conversion of coal and petroleum heavy oil fractions to produce distillate liquid products while upgrading the remaining heavy oil merits further investigation. This type of process, termed, coal/oil coprocessing has the potential for being an effective method for converting coal to liquids and for introducing coal liquids into the market place in a cost effective evolutionary manner while greatly reducing the capital investment associated with the historical approach for establishing a liquefaction industry. Among the additional potential benefits for the implementation and utilization of the coprocessing concept are:

a) Provision of a link or bridge between present day refining technology and a total coal based synfuels industry.

b) Improved economics compared to direct coal liquefaction due to smaller plant sizes, due to lower hydrogen requirements and the elimination of the use of process derived solvent recycle.

c) Residuum demetallization, improved product yields and mix.

d) Minimization of the production of gases and undesirable by-products; such as high sulfur coke.

e) Continued use of the U.S. hydrocarbon fuel infrastructure.

f) A means of extending petroleum reserves by reducing crude utilization requirements.

Coprocessing Schemes

The coprocessing schemes under consideration are generally an extension of two-stage coal liquefaction and application of residuum hydrocracking technology. It has been recognized that a possible synergism exists between coal derived liquids and petroleum derived residua. Coprocessing improves the quality of synthetic liquid fuel products from coal by diluting them directly with petroleum-derived liquids. Coal liquids contain a much higher proportion of aromatics compared to conventional petroleum-derived liquids, and the non-aromatic portion tends to be naphthenic rather than paraffinic. Coal liquids contain significant amounts of highly-polar compounds, and asphaltenes, but a relatively low amount of sulfur containing compounds.

Further, petroleum-derived naphtha, is low in nitrogen and oxygen. Coal-derived naphtha, on the other hand, has higher nitrogen and oxygen contents, is easier to reform, and has a higher octane number. Thus, combining coal-derived liquids with petroleum-derived liquid can provide some positive impacts on the overall product quality.

Broadly speaking, the coprocessing processes can be divided into four categories:

o Hydro-catalytic processes
o Extractive processes
o Thermal processes (non-catalytic)
o Hydro-thermal processes

The first category includes HRI, Lummus, CANMET, UOP, Chevron and Kerr-McKee processes. The second category includes processing variations incorporated for solids removal and deasphalting by Kerr-McGee, UOP and Lummus. The Cherry-P-process falls into the thermal process category. The process conditions are somewhat between those visbreaking and delayed coking. The Pyrosol process falls into the last category above and utilizes a mild hydrogenation of coal and heavy oil in the first stage. The second stage processes residuum under hydrogen pressure to produce more oil.

Refinery Integration Considerations

Since the late 1970's intensive capital investments in residuum upgrading and hydrotreating capacity have been made by the refinery industry for the conversion of heavier crude oil fractions to gasoline and distillate fuels. At the same time, the number of operating refineries in the United States has decreased from 319 to 191. As shown in Figure 1, this decrease has been accomplished primarily by the deactivation of a number of low capacity refineries operating in the hydroskimming or topping mode. The major driving force for this realignment in refining capacity has been largely due to a growing imbalance between the residuum content of available crude oil and a decrease in demand for residual fuel oil. Residual fuels such as No. 6 Fuel Oil, Bunker C, etc., are by-products of refining. As such, their production and availability are based on the demand for transportation and distillate fuels. Based upon data in the Oil and Gas Journal, residuum processing (thermal and hydrocracking) capacity as a percent of overall refining capacity has essentially increased 20% since 1980 to provide supply elasticity for the changing residual fuel demand, representing about 19% of the today's U.S. crude processing capacity. The future outlook is for this trend to continue as fuel oil is replaced by other energy forms such as coal, nuclear and natural gas. It is important to note that this processing of the heavy ends to yield prime products represents a reduction in the amount of crude oil required to meet gasoline and distillate fuel demand. Table 1 presents a profile of the Refining Industry in the U.S.
While coal liquefaction research and development has demonstrated significant progress in recent years, it has not addressed the fundamental causes for the high

cost of coal liquefaction, the high recycle oil requirements. In all direct liquefaction processes coal is slurried with a process derived recycle oil at a ypical ratio of 2:1 recycle oil to coal feed. Coprocessing of residuum and coal reduces the high cost associated with recycle oil by eliminating or reducing the requirements for recycle oil.

Coprocessing hydrocracking technology was originally developed for processing heavy crude with coal additives as a means of inhibiting the formation of coke. The CANMET hydrocracking process is based upon this comcept. This emerging technology shows promise of high demetallization, residuum hydrocracking, and high conversion of the pitch (975^{0}F^{+}) fraction. Coal additives include 1.0 - 2.0 wt.% of fine coal and ferrous sulfate.

Integration of the CANMET type process initially to an existing refinery and/or idle units is a first step toward utilization of coal and heavy oils (pitch and asphaltenes). A once through process arrangement without the use of a recycle stream may also be possible at lower coal concentrations.

Coprocessing technologies to be included in a staged approach are HRI, Lummus, and the Cherry-P processes which can process up to 50 wt.% of coal in heavy oil fraction.

Implementation of coprocessing will likely require additional refinery hydrogen generation. This will probably be based upon steam reforming of hydrocarbon gases and light naphtha. Steam reforming is a well established and adopted method of generating hydrogen. The expansion of reforming units can be accomplished more easily than integrating gasification units into refineries.

Hydrostabilization of product distillates are incorporated into a refinery to provide hydrotreatment and product stabilization prior to distribution outside the refinery complex. Further pretreatments for heteroatom removal may be required in a refinery utilizing coprocessing derived liquids.

The introduction of coal/residuum coprocessing will tend to reduce crude requirements. The extent of reduction will be dictated by market demands as well as product yields and qualities of the coprocessing distillate liquids. Other positive factors are 1) the use of existing refinery and infrastructure, 2) better economics than direct liquefaction, 3) compatability with the use of heavier crudes, and 4) the capability of installing a coprocessing unit independently from existing refinery operations.

Potential Coal Requirements

An estimate of the potential coal requirements for coal/oil coprocessing for the general refinery types in the United States is presented in Table 2. These capacities represent an upper limit for the application of coal/residua coprocessing as fuel oil production was assumed to be zero. It was also assumed that coprocessing is more economic than vacuum distillation (both cases are highly unlikely). Based upon a 1985 production capacity of 890 million tons of coal in the U.S.; coal producing capacity would have to increase by one-third if the upper limits of coal/residua coprocessing were achieved.

The most likely near term application for coal/oil coprocessing appears to be for residuum conversion capacity additions to low conversion refineries to improve profitability and to high conversion refineries to provide the capability for handling future feedstocks with increasingly higher residuum content. This premise is based on the assumption that present trends toward a heavier crude feedstocks and lighter reduced fuel oil requirements will continue. In terms of refinery capacity, average size Hydroskimming or Topping and High Conversion Refineries

processing 25,000 and 150,000 bbl/day of heavy crude (25° API), respectively, will require approximately 850 and 4,000 tons/day of coal, respectively, when coprocessing at slurry concentrations of 50%. These coal capacities are well within existing transportation and handling experience for coal fired industrial/utility boiler applications.

Process Economics

While the detailed engineering required to develop definitive coprocessing economics was beyond the scope of the effort, this paper would not be complete without presenting some guidelines. For this purpose, the installation of a coprocessing plant with a residuum throughput of 10,000 bbl/day (600-700 tons/day of coal) to a refinery (Figure 2) is estimated to cost of the order of $170MM. This cost includes coal handling and preparation, coal/residuum conversion and allowances for hydrocarbon steam reforming for hydrogen generation ($\sim$ 40% of the cost). Land and owner costs are not included in the estimate. In addition, it must be stressed that actual costs are refinery specific and will vary greatly, depending upon the adequacy and availability of refinery utility systems and the degree of integration capability.

Development Program Requirements

A potentially broad variety of coals and petroleum residua are candidates for coprocessing. The properties of these feedstocks will have to be investigated in bench scale experiments to define product quality. In addition, better characterization of hydrogen requirements are required to improve economies. These data are required to facilitate the design and integration of coprocessing units into existing refineries.

Conclusions

Although continued Research and Development are required to define product quality and yields, coprocessing of coal and residual oil shows promise. It is anticipated that initial application of coprocessing will involve the utilization of small amounts of coal (1-2 wt.%) in existing refineries. This will be followed by demonstration units (10,000-15,000 bbl/day) utilizing a staged approach, processing 30-40 wt.% coal. Commercial units should be able to process up to 50-60 wt.% coal and will be integrated into high and low conversion refineries using vacuum residua as feedstocks and that there is a potential for the installation of upwards of 100 units of 10-15,000 bbl/day capacity.

TABLE 1

OIL REFINING PROFILE (CONTINENTIAL USA)

	Hydroskimming	Low Conversion	High Conversion	Specialty Plants
Number of Refineries	24	59	61	41
Capacity, K BBL/day	560	4,685	9,215	475
% Capacity	4	31	62	3
Major's Operate, %	30	25	90	Low

Source - Oil and Gas Journal

TABLE 2

IMPACT OF CONVERSION OF EXISTING REFINERY
CAPACITY TO ADVANCED COPROCESSING OF FUTURE HEAVY CRUDES

	Coal Consumption, MMTY	
	Feedstock	
Existing Refinery Type	Atmospheric Residuum	Residuum
Hydroskimming	9 - 11	3 - 6
Low Conversion	74 - 94*	30 - 50
High Conversion	146 - 185*	58 - 99*
	229 - 290	91 - 155

* Requires Shutdown of Existing Units
--Prime Application for Coprocessing

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FIGURE 1

DISTRIBUTION OF REFINERIES BY SIZE
1980 to 1985

NUMBER OF REFINERIES

Legend:
1980
1981
1982
1983
1984
1985

(y-axis values: 0, 12, 24, 36, 48, 60, 72, 84, 96, 108, 120)

THOUSAND BARRELS PER DAY

(x-axis categories: 0–10, 10–30, 30–60, 60–100, 100–175, 175+)
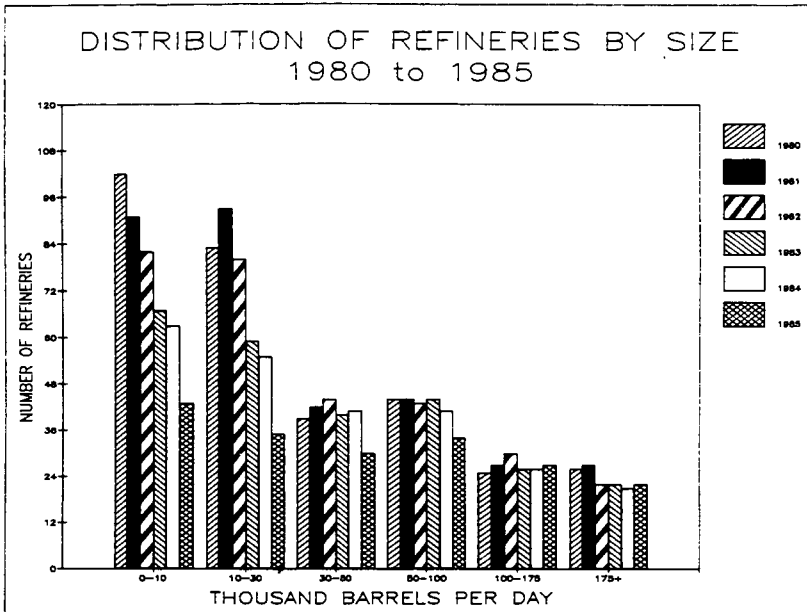
FIGURE 2
FLOW DIAGRAM
HIGH CONVERSION REFINERIES WITH COPROCESSING

CAT REF
C4
SAT LT ENDS REC
C2 — TO FUEL GAS
C3 — LPG PLANT FUEL
C4 — MOGAS PLANT FUEL ALKYLATION
LNV — HYDRO TREAT — MOGAS
INV — CAT REF H/T — CAT REF — C5 TO MOGAS
C4 TO SAT LT ENDS
H2 RICH GAS TO H/T

CRUDE — ATMOS P/S
KERO — KERO H/T — TO JET DIESEL HEATING OIL
LAGO — AGO H/T — LAGO
HAGO — HAGO — TO DIESEL AND HEATING OIL

CAT LT ENDS
C2 FUEL GAS LPG
C3/C4 ALKY
nC4 — MOGAS
ALKYLATE MOGAS
C4 FROM SAT LT ENDS AND PURCHASES

VAC P/S — VGO — CAT FD H/T
GAS OIL C4
CAT CRACKER
NAPHTHA — MOGAS
DISTILLATE
HEATING OIL DIESEL

COAL

COPROCESSING UNIT
LT NAPH — H/T — MOGAS
HY NAPH — H/T — CAT REF
FUEL OIL, PLANT FUEL
PITCH

LEGEND:
LVN = LIGHT VIRGIN NAPHTHA
IVN = INTERMEDIATE VIRGIN NAPHTHA
LAGO = LIGHT ATMOSPHERIC GAS OIL
HAGO = HEAVY ATMOSPHERIC GAS OIL
VGO = VACUUM GAS OIL
P/S = PIPESTILL
H/T = HYDROTREATER

NOTE:
HYDROTREATERS IN DASHED BOXES ARE NOT REQUIRED FOR LOW SULFUR CRUDE. NOT SHOWN ARE SULFUR RECOVERY, HYDROGEN GENERATION AND HYDROGEN RECOVERY PROCESS FACILITIES

CHEMICAL AND TOXICOLOGIC CHARACTERIZATION OF CO-PROCESSING AND TWO-STAGE DIRECT COAL LIQUEFACTION MATERIALS

Cherylyn W. Wright, Dorothy L. Stewart, D. Dennis Mahlum,
Edward K. Chess, and Bary W. Wilson

Pacific Northwest Laboratory
P. O. Box 999
Richland, WA 99352

INTRODUCTION

Research and development of advanced coal liquefaction technology is being supported by the U.S. Department of Energy (DOE) as a means of utilizing domestic supplies of coal to produce petroleum-substitute fuels. As a component of this effort, the U.S. DOE has supported the chemical analyses and toxicological evaluations of coal conversion products and internal process materials to assess the potential health effects and industrial hygiene concerns associated with coal liquefaction technology.

Recent advances in coal liquefaction have included two-stage direct coal liquefaction processes and petroleum resid/coal co-processing technology. Two-stage coal liquefaction processes are generally comprised of a first-stage thermal or liquefaction reactor followed by a second-stage hydrogenation step. Petroleum resids and coal are simultaneously converted to liquefaction products in co-processing technology. The purpose of this paper is to report the preliminary results of the chemical analysis and toxicological testing of a coal liquefaction co-processing sample set, and to compare these results to those obtained from two-stage coal liquefaction materials.

SAMPLES

Samples for comparative chemical analysis and toxicological evaluation were provided from the proprietary UOP, Inc. co-processing technology (Des Plaines, Illinois) and the integrated, non-integrated, reconfigured integrated, and close-coupled reconfigured integrated two-stage coal liquefaction processes (ITSL, NTSL, RITSL, and CCRITSL respectively) from the Wilsonville Advanced Coal Liquefaction Research and Development Facility (Wilsonville, Alabama) operated by Catalytic, Inc. A summary is contained in Table 1 of the co-processing samples received from UOP, Inc. and the two-stage coal liquefaction materials analyzed for comparative purposes. Since the samples provided were from pilot plant or bench-scale advanced coal liquefaction origins, they may not necessarily be representative of materials produced on a commercial basis.

A description of the proprietary UOP, Inc. catalyzed, slurry, single-stage coal liquefaction co-processing technology has been given by Gatsis, *et al*. (1). ITSL and NTSL processes have been described by Later (2). For a brief overview of the RITSL and CCRITSL, see Gough *et al* . (3).

EXPERIMENTAL

Samples were chemically characterized by chemical class fractionation, gas chromatography, gas chromatography-mass spectrometry, and low-voltage probe-inlet mass spectrometry. Toxicological activity was measured using the standard histidine reversion microbial mutagenicity test and an initiation/promotion assay for mouse skin tumorigenesis. A brief description of these methods follow.

Chemical Class Fractionation

Samples were fractionated according to the method described by Later *et al* . (4) and Later and Lee (5) by sequential elution of standardized alumina (1.5% water, Later *et al.*, 6) with 20 ml hexane, 50 ml

Table 1. Samples Analyzed

PNL Number	Process	Description
51396-005	UOP	Lloydminster Petroleum Resid. Nominal boiling point (bp) >840°F, including non-distillables, no solids.
51396-004	UOP	Illinois No. 6 Coal and Lloydminster Petroleum Resid Slurry Feed. Nominal bp >840°F, including solids and non-distillables.
51396-001	UOP	Liquid Process Solvent (LPS). Nominal bp >212°F, including solids and non-distillables.
51396-003	UOP	Vacuum Fractionator Overhead Product. Nominal bp ~212-910°F.
51396-002	UOP	Vacuum Fractionator Bottoms Product. Nominal bp >910°F, including solids and non-distillables.
5226-059	ITSL	Hydrotreater (HTR) Distillation Column Bottoms. Nominal bp ~450-850°F. Run #242.
5226-022	NTSL	HTR Distillation Column Bottoms. Nominal bp ~450-850°F. Run #241.
50378-100	RITSL	HTR Heavy Distillate Product. Nominal bp >500°F, including resids and ash. Run #247.
50378-101	RITSL	HTR Heavy Distillate Product. Nominal bp >500°F, less resids and ash. Run #247.
50378-139	CCRITSL	HTR Heavy Distillate Product. Nominal bp >500°F. Run #249.

benzene, 70 ml chloroform:ethanol (99:1), and 50 ml methanol to produce aliphatic hydrocarbon (AH), polycyclic aromatic hydrocarbon (PAH), nitrogen-containing polycyclic aromatic compound (NPAC), and hydroxy-substituted PAH (hydroxy-PAH) fractions, respectively. The weight percent contribution of each fraction was determined gravimetrically after solvent removal by rotoevaporation at 40°C and drying under a stream of nitrogen.

Gas Chromatography

Selected fractions were analyzed by gas chromatography using a Hewlett-Packard (HP) 5880A gas chromatograph equipped with a 30-m x 0.25-mm-ID fused silica capillary column coated with 0.25-μm film thickness DB-5 (J & W Scientific). The oven was temperature-programmed to 280°C at 4°C/min after 2 minutes isothermal at 50°C with a 5 minute isothermal period at the upper temperature limit. Splitless injection was used with hydrogen as carrier gas at 100 cm/sec linear velocity. The injection port and flame ionization detector were operated at 275 and 300°C, respectively. Fractions were analyzed at 5.0 mg/ml dilutions with 2-chloroanthracene added as an internal standard at a final concentration of 25 ng/μl.

Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS analyses were performed on an HP-5982A quadrupole mass spectrometer interfaced to an HP-5710 gas chromatograph equipped with a 15-m x 0.25-mm-ID DB-5 fused silica capillary column (J & W Scientific). Gas chromatographic conditions were similar to those described above, except the oven was temperature-programmed at 8°C/min. The MS was operated in the electron impact mode at 70 eV, and scan rates were typically 100 atomic mass units (amu)/sec.

Low-Voltage Probe-Inlet Mass Spectrometry (LVMS)

A VG ZAB 2-F double-focusing MS operated in the electrom impact mode using ionizing electron energies of 10-12 eV was used for the LVMS analyses. Each sample (10 to 20 μg) was loaded into a glass capillary tube, which was then inserted into the source affixed to the end of a direct insertion probe. The probe was heated in a linear fashion from ambient to 250-280°C while the MS scanned repeatedly throughout the desorption period. The MS was operated with an accelerating voltage of 6000 or 7000 V, a magnet scan rate of 2 to 3 sec/mass decade, a source temperature of 250°C, and a dynamic resolving power (as determined by the VG 2035 data system) of 1:2000. The intensities of each mass across the entire profile were summed, generating an average spectrum that was representative of the entire sample.

<u>Microbial Mutagenicity</u>

Standard agar-plate mutagenicity assays were perfomed as described by Ames *et al.* (7) using *Salmonella typhimurium*, TA98 microbial tester strain with S9 metabolic activation. Revertant colonies per petri plate were counted using a Biotran II automated colony counter. The specific mutagenic activities of samples are expressed as revertant colonies of *S. typhimurium*, TA98 per μg of test material as estimated by linear regression analysis of dose-response data. The following criteria were used for selecting the best dose range for estimating a linear dose response: at least a four-point dose range; approximate doubling of response for doubled dose concentration; a correlation coefficient of 0.8 or greater; and an intercept on the response (ordinate) axis within 20% of the negative control for the day.

<u>Initiation/Promotion (I/P) Assay for Mouse Skin Tumorigenicity</u>

The I/P mouse skin tumorigenicity assays were performed on selected samples as described by Mahlum (8) using female CD-1 mice (Charles River Laboratories, Portage, MI), approximately 6 to 8 weeks of age with 30 animals per test group. Each test material was diluted 1:1 with acetone or methylene chloride, and 50 μl of the diluted material was applied to the shaved backs of the mice (approximately 25 mg dose per mouse). Two weeks after initiation, 5-μg doses of phorbol myristate acetate (0.1 mg/ml acetone) were applied to the initiated area, twice weekly for 24 weeks. The mice were shaved as necessary throughout the study, usually weekly. Animals were observed regularly for tumor growth, and the number of tumors per animal was counted biweekly. The data are expressed as the total number of tumors per mouse normalized to groups of 30 mice.

RESULTS AND DISCUSSION

The results of the chemical class fractionation by alumina column chromatography are given in Table 2 for the advanced coal liquefaction products and internal process materials studied. The Lloydminster petroleum resid and the slurry feed from the UOP co-processing technology had low levels of AH compared to the other materials fractionated using these methods. The UOP slurry feed also gave a lower total recovery of material from the neutral alumina than did the other materials, indicating there was a high concentration of insoluble or intractable components in the slurry feed presumably due to the presence of

Table 2. Chemical Class Fractionation Data

Sample[b]	Process	Fraction Weight Percent[a]				
		AH	PAH	NPAC	Hydroxy-PAH	Total
51396-005	UOP	12	50	36	3	101
51396-004	UOP	8	26	22	2	58
51396-001	UOP	26	26	23	10	85
51396-003	UOP	53	27	8	6	94
51396-002	UOP	19	27	30	11	87
5226-059	ITSL	63	26	5	9	103
5226-022	NTSL	45	34	7	15	101
50378-100	RITSL	58	36	4	2	100
50378-101	RITSL	57	39	4	2	102
50378-139	CCRITSL	60	43	5	4	112

[a]Average of two determinations
[b]For description, see Table 1

the coal itself. The chemical composition of the UOP vacuum fractionator overhead product (51396-003) was comparable to an average composition of the two-stage coal liquefaction products, as determined by this chemical class fractionation. The UOP bottoms product had a decreased AH composition and an increased NPAC and hydroxy-PAH content compared to the lower boiling UOP overhead product. Similar results have been noted for both single- and two-stage coal liquefaction materials, namely, that higher boiling fractions have had decreased AH content and increased heteroatom content compared to their lower boiling counterparts (9).

The PAH fractions isolated from the samples were analyzed in greater detail since this chemical fraction has historically been the most tumorigenic fraction isolated from coal liquefaction products and internal process materials when analyzed using these methods. High-resolution gas chromatograms of the PAH fractions isolated from the UOP, ITSL, and NTSL distilled products are shown in Figure 1. Many of the major components in each of these fractions are labelled with their identifications from retention time and GC/MS data. The major components identified in the UOP vacuum fractionator overheads were similar to the major components identified in both the ITSL and NTSL hydrotreater distillation column bottoms; PAH compounds were present ranging from two to four aromatic rings in size. Alkyl-substituted PAH and some hydroaromatics (particularly of m/z 168 and 182, the parent and methyl-substituted dihydrofluorenes or dihydrophenalenes) were also detected in all three products. The components identified in the RITSL and CCRITSLPAH fractions were similar to those detected in the UOP, ITSL, and NTSL PAH fractions of Figure 1, except they were of a higher molecular weight range; the methylchrysene isomer was the component of highest concentration in both the RITSL and CCRITSL distilled products.

The LVMS spectra from the analyses of the PAH fractions isolated from the UOP, ITSL, and NTSL distilled products are shown in Figure 2. The UOP product PAH fraction was more complex than either of the two-stage coal liquefaction PAH fractions shown. For example, there were signals for a greater number of masses representing 40% or more of the total ion current (TIC) in the UOP product PAH fractions than there were for the ITSL and NTSL PAH fractions. There was also relatively more materials that gave rise to the series including masses 232, 246, 260, and 274 amu in the UOP distilled product PAH fractions as compared to the ITSL and NTSL distilled product PAH fractions, showing some differences in the composition of the co-processing and two-stage coal liquefaction samples.

Table 3 contains the results of microbial mutagenicity testing of the crudes and chemical class fractions isolated from some of the advanced coal liquefaction samples studied. No mutagenic activity was detected in any of the AH or PAH fractions isolated from the UOP petroleum resid/coal co-processing materials, as was also the case for the distilled two-stage coal liquefaction products. Regardless of process, the majority of the microbial mutagenicity was expressed by the isolated NPAC fractions, with

Table 3. Microbial Mutagenicity Data

| Sample[a] | Process | Response (rev/μg); Chemical Class Fraction | | | | |
		Crude	AH	PAH	NPAC	Hydroxy-PAH
51396-004	UOP	0	0	0	0	<1
51396-001	UOP	6	0	0	10	4
51396-003	UOP	4	0	0	48	2
51396-002	UOP	3	0	0	6	6
5226-059	ITSL	0	0	0	3	0
5226-022	NTSL	6	0	0	65	<1
50378-100	RITSL	0	0	0	22	3
50378-101	RITSL	4	0	0	32	0

[a]For description, see Table 1

some mutagenic response also expressed by the hydroxy-PAH fractions (particularly in the UOP vacuum fractionator bottoms product, 51396-002). The microbial mutagenic response of the UOP vacuum fractionator overhead product more closely resembled the response of the NTSL and RITSL distilled products, showing increased mutagenic activity as compared to the ITSL distilled product.

Initiation/promotion results, given as total number of tumors per mouse ± standard error, for the ITSL and NTSL hydrotreater distillation column bottoms were 1.3 ± 1.2 and 1.1 ± 1.4, respectively.

ACKNOWLEDGMENTS

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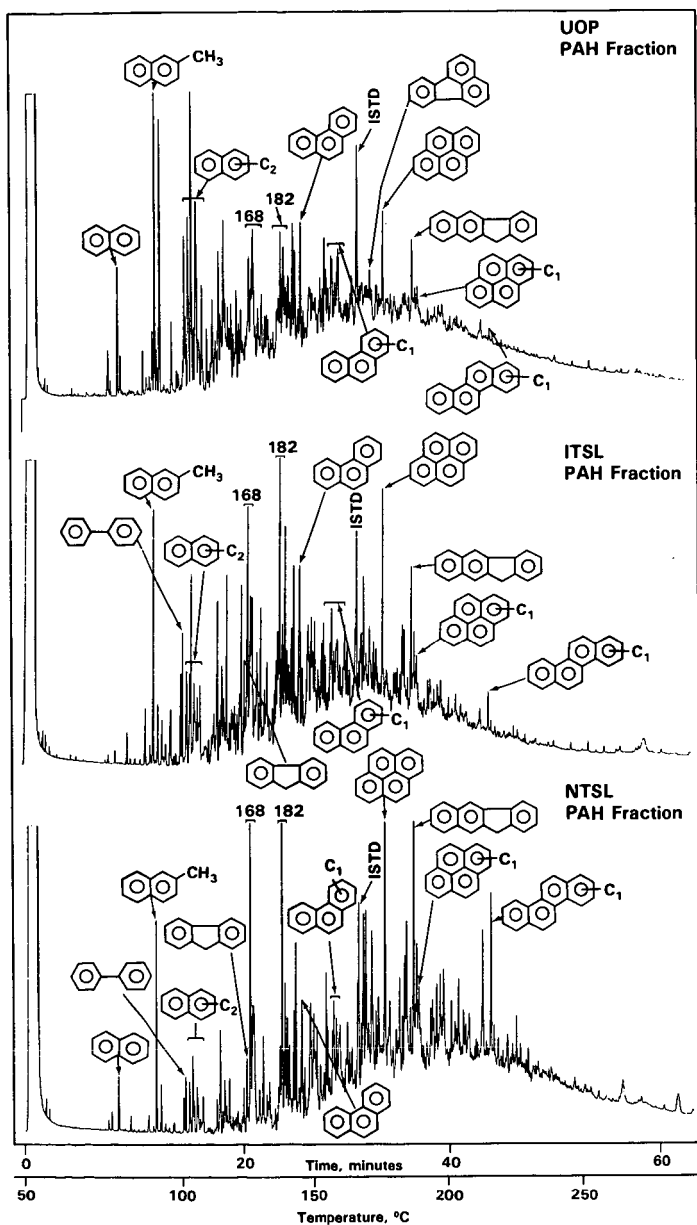
Figure 1. High Resolution Gas Chromatograms of the PAH Fractions Isolated from the UOP Vacuum Fractionator Overhead Product (top), ITSL (middle) and NTSL (bottom) Hydrotreater Distillation Column Bottoms. See Text for Conditions.
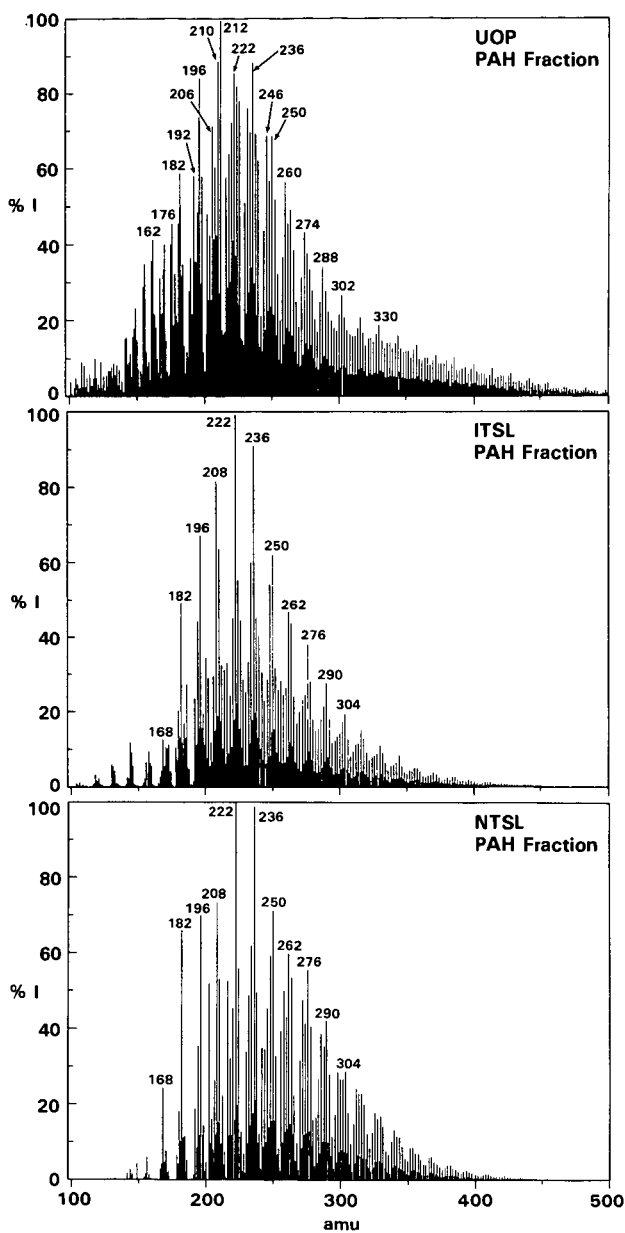
Figure 2. LVMS Spectra. See Figure 1 for Sample Descriptions. See Text for Conditions.

PROCESS DEVELOPMENT STUDIES OF
TWO-STAGE LIQUEFACTION AT WILSONVILLE

C. W. Lamb, R. V. Nalitham

Catalytic, Inc., Wilsonville, AL   35186

and T. W. Johnson

Southern Company Services, Inc., Wilsonville, AL   35186

INTRODUCTION

The Advanced Coal Liquefaction R&D Facility at Wilsonville, Alabama, has been in operation
for over 12 years. It is the largest direct coal liquefaction pilot plant still in
operation in the United States. Process investigations have evolved from the original
study of the Solvent Refined Coal Process for making a clean solid fuel to the recent
investigation of two-stage liquefaction processes for making clean distillate fuels. This
paper presents results from the current study of various processing schemes designed to
reduce the cost of fuels produced by two-stage liquefaction plants.

Most important among these configurations is direct coupling of the thermal and catalytic
reactors. Such close-coupled operation should lower the cost of two-stage fuels by
increasing overall thermal efficiency and improving product quality. Results from
Wilsonville runs are characterized by discussion of representative product yield and
product quality data. Also, a comparison of performance and stability of Shell 324 and
Amocat 1C catalysts is presented.

Other pertinent tests in the close-coupled mode are discussed with particular emphasis on
the effect of higher system space velocity and on the impact of solids recycle.

PROCESS CONFIGURATION COMPARISON

The integrated TSL (ITSL) mode and the close-coupled (CC-ITSL) mode are shown in Figures 1
and 2, respectively. In both modes, the reaction stages are integrated by the recycle of
hydrotreated resid with the goal of producing "all-distillate" yield slates. The CC-ITSL
configuration differs from ITSL in that for the CC-ITSL mode, products from the thermal
reactor are fed directly to the catalytic reactor without pressure letdown or significant
cooling. Accordingly, vacuum-flashed product from CC-ITSL is deashed downstream of the
catalytic reactor rather than upstream as in the ITSL mode. Close-coupled operation thus
eliminates thermal inefficiency of the cool down/reheat cycle associated with deashing
between reaction stages.

PROCESS PERFORMANCE

A wide range of thermal and catalytic stage operating conditions were investigated in the
CC-ITSL mode to determine their effects on product yield structure and quality. For
comparison purposes, Table 1 lists five sets of CC-ITSL conditions and yields relative to
one typical set of ITSL conditions and yields. Illinois No. 6 coal from Burning Star Mine
was used in all the runs.

An initial baseline run (250B) was conducted using aged Shell 324 catalyst to quantify the
impact of coupling the reactors. No interstage vapor separation was utilized in Run 250B,
although a high pressure separator was installed and operated during the remainder of the
run. The major effect of close-coupled operation was an increase in hydrogen consumption
with a corresponding improvement in distillate product quality (Table 2). Hydrogen and
sulfur values were significantly better for CC-ITSL (250B) when compared to ITSL (244).
This improvement resulted from the fact that all the TSL product was derived from the

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catalytic stage in Run 250B, whereas in Run 244 approximately 45 wt % was produced by the catalytic hydrotreater (Table 3). Higher quality products are made by the catalytic stage.

Subsequent operation in CC-ITSL was devoted to study of performance of a new catalyst, Amocat 1C. As noted previously, interstage vapor separation was employed throughout this period. A comparison of "all-distillate" operation at the same coal feed rate for Shell 324 and Amocat 1C revealed that distillate and hydrocarbon gas yields were similar (Run 250B versus Run 250C). An alternate deashing solvent was used in Run 250C in order to maintain stable performance while processing the highly soluble feed generated by the fresh Amocat catalyst. This resulted in greater rejection of resid to ash concentrate with concommitantly less TSL resid produced. A lower hydrogen consumption was observed for Run 250C. This phenomenon could be attributed to the effect of interstage separation (i.e., not hydrotreating all distillate products) and/or to relatively lower hydrogenation activity of the Amocat catalyst.

Higher system space velocities were explored by increasing coal feed rates. The goal was to demonstrate the production of high quality (CC-ITSL) distillates at reduced cost. Yield data are reported for Run 250 Periods C, D, and E in Table 1. Product quality data and unit contributions to distillate production for Period D are given in Tables 2 and 3, respectively. The data clearly indicate that "all-distillate" yield slates were produced at increased throughputs by compensatory increases in reactor temperatures. Product quality did not change significantly at the higher rates. It should also be noted that products from higher space velocity CC-ITSL were substantially better than those from lower space velocity ITSL.

Near the conclusion of Run 250, a test of solids (unconverted coal and ash-cresol insolubles) recycle was performed (Figure 3). The objective was to decrease size of the critical solvent deashing unit by deashing a higher solids content vacuum bottoms stream. Deashed resid was recycled as a component of the liquefaction solvent. Lower organic rejection to the ash concentrate was demonstrated with the concentrated feed. Based on this result, the concept of solids recycle may be investigated in a future close-coupled run using catalyst in both reactors.

Batch deactivation trends for resid conversion in the catalytic reactor were developed for the ITSL (deashed bituminous)- Shell 324 and CC-ITSL (close-coupled bituminous)-Amocat 1C modes, using a first order resid conversion model (1). The trends are plotted in Figure 4 together with batch deactivation data from Wilsonville Run 247 ("simulated" close-coupled). The trends showed initial periods of rapid deactivation, followed by slower deactivation rates. Higher resid conversion rate constants were observed for close-coupled operation using the Amocat 1C catalyst. The close-coupled resid/Amocat combination was more reactive than the other feed/catalyst (Shell 324) combinations. Figure 5 further illustrates this point in an Arrhenius plot.

RELATIVE ECONOMICS

Results from an economic screening study performed by Lummus Crest Inc. indicated a reduction in the required product selling price for CC-ITSL products compared to ITSL products (Table 4). The study was based on a conceptual commercial 10,000 TPD plant using Illinois No. 6 coal. The relatively lower price was due to higher distillate production and improved distillate quality for the close-coupled case (2).

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SUMMARY

- The major effect of close-coupled operation was an increase in hydrogen consumption with a corresponding improvement in distillate product quality.

- At the same coal feed rate, C_4+ distillate and hydrocarbon gas yields were similar for close-coupled operation with Shell 324 and Amocat 1C catalysts. A lower hydrogen consumption was observed in the Amocat operation. This phenomenon could be attributed to the effect of interstage separation and/or to the relatively lower hydrogenation activity of the Amocat catalyst.

- "All-distillate" yield slates were produced at higher system space velocities by compensatory increases in reactor temperatures.

- Product quality was not significantly affected at higher system space velocities.

- Operating with solids recycle in the close-coupled mode, lower organic rejection to ash concentrate was demonstrated at a relative reduction in feed rate to the critical solvent deashing unit.

- A comparison of resid conversion rate constants indicated that the close-coupled resid/Amocat 1C combination was more reactive than other feed/catalyst (Shell 324) combinations.

- Results from an economic screening study for a conceptual commercial 10,000 TPD plant indicated a reduction in the required product selling price for CC-ITSL plant products compared to ITSL plant products.

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Table 1

PROCESS CONDITIONS AND YIELDS

Configuration Run No. Catalyst Type	ITSL 244 Shell 324	CC-ITSL(1) 250B Shell 324	CC-ITSL(2) 250C Amocat 1C	CC-ITSL(2) 250D Amocat 1C	CC-ITSL(2) 250E Amocat 1C	CC-ITSL(2) 250F Amocat 1C
Thermal Stage						
Reactor temperature (°F)	810	810	810	825	830	835
Coal space velocity [lb/hr-ft^3 (>700°F)]	28	25	25	37	45	37
Inlet H$_2$ partial pressure (psi)	2040	2800	2380	2380	2380	2380
Solvent-to-coal ratio	1.8	1.8	1.8	1.8	1.8	1.9(5)
Catalytic Stage						
Reactor temperature (°F)	730	730	700	740	750	760
Space velocity (lb feed/hr-lb cat)	1.0	1.0	1.3	2.1	2.6	2.2
Catalyst age (lb resid/lb cat)	1070	1450(3)	350(3)	750(3)	1100(3)	550(3)
TSL Yield(4)(% MAF Coal)						
C$_1$-C$_3$ Gas	6	6	5	7	6	8
C$_4$+ Distillate	57	61	61	64	58	62
Resid	7	6	2	-2	7	7
Ash Concentrate (ash-free)	20	18	22	22	19	15
Hydrogen Consumption	-5.4	-6.5	-5.6	-6.1	-5.7	-6.5

(1) Without interstage vapor separation.
(2) With interstage vapor separation.
(3) Catalyst age is (lb resid + ash + unconverted coal)/lb catalyst.
(4) Elementally balanced yield structure.
(5) Recycle solvent contains unconverted coal and ash (cresol insolubles-CI).

Table 2

PROPERTIES OF DISTILLATE PRODUCTS

Distillation Cut	Wt % of Crude	Elemental (Wt %)				
		C	H	N	S	O (diff)
ITSL (Run 244)(1)						
Naphtha (IBP-350°F)	18.6	85.21	12.86	845 ppm	0.36	1.50
Distillate (350-650°F)	46.1	86.34	10.73	0.23	0.22	2.48
Gas Oil (650°F+)	35.3	89.07	9.69	0.31	0.16	0.76
CC-ITSL (Run 250B)(2)						
Naphtha (IBP-350°F)	19.0	85.31	14.51	0.17	0.01	-
Distillate (350-650°F)	46.8	87.43	12.12	0.21	0.06	0.18
Gas Oil (650°F+)	34.2	88.41	10.88	0.57	0.04	0.10
CC-ITSL (Run 250D)(3)						
Naphtha (IBP-350°F)	18.6	85.35	14.25	0.22	0.18	-
Distillate (350-650°F)	45.0	87.45	11.73	0.32	0.09	0.41
Gas Oil (650°F+)	36.4	88.77	10.27	0.43	0.07	0.46

(1) Samples obtained with catalytic stage temperature of 730°F, space velocity of 1.0 lb feed/hr-lb catalyst, and catalyst age of 1400 lb resid/lb catalyst (Shell 324).

(2) Samples obtained with catalytic stage temperature of 730°F, space velocity of 1.0 lb feed/hr-lb catalyst, and catalyst age of 1450 lb (resid + ash + unconverted coal)/lb catalyst (Shell 324).

(3) Samples obtained with catalytic stage temperature of 740°F, space velocity of 2.1 lb feed/hr-lb catalyst, and catalyst age of 750 lb (resid + ash + unconverted coal)/lb catalyst (Amocat 1C).

Table 3

UNIT CONTRIBUTIONS TO DISTILLATE PRODUCTION

Configuration	ITSL	CC-ITSL[1]	CC-ITSL[2]
Run No.	244	250B	250D
Catalyst Type	Shell 324	Shell 324	Amocat 1C

Unit Contributions[3]

Thermal Stage	55	0	25
Catalytic Stage	45	100	75

(1) Without interstage vapor separation.
(2) With interstage vapor separation.
(3) Wt % of total distillate production.

Table 4

ECONOMIC SCREENING STUDY[1]
(10,000 TPD PLANT)

	ITSL (BASE)	CC-ITSL
Relative Capital Cost	1.00	1.04
Relative Operating Cost	1.00	1.01
Relative Production Rate[2]	1.00	1.10
Relative Required Product Selling Price[3]	1.00	0.93
Thermal Efficiency (%)	68.1	69.6

(1) Performed by Lummus Crest, Inc. under EPRI RP832-11.
(2) Based on barrels of crude oil equivalent with consideration for quality of distillate products.
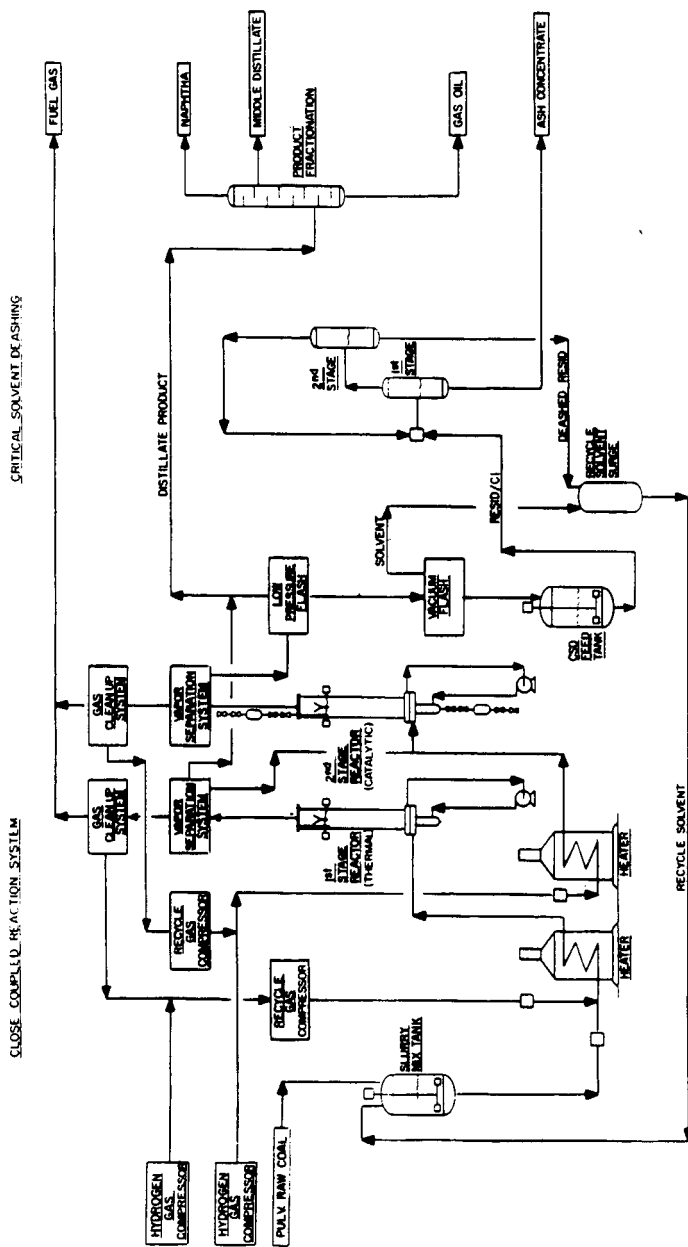(3) First year.

FIGURE 1: INTEGRATED TWO STAGE LIQUEFACTION SYSTEM
INTER-STAGE DEASHING

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FIGURE 2: CLOSE COUPLED INTEGRATED TWO STAGE LIQUEFACTION SYSTEM
THERMAL – CATALYTIC WITH INTER-STAGE VAPOR SEPARATION

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CRITICAL SOLVENT DEASHING

CLOSE COUPLED REACTION SYSTEM
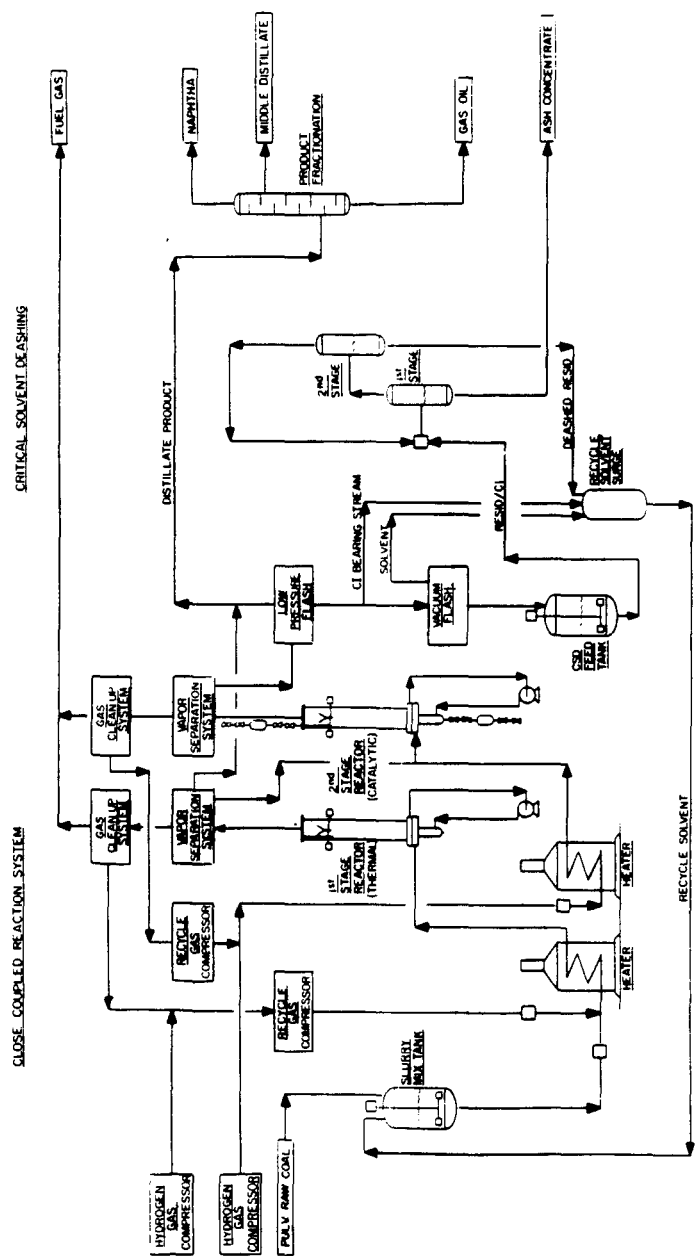
FIGURE 3. CLOSE COUPLED INTEGRATED TWO STAGE LIQUEFACTION SYSTEM
THERMAL - CATALYTIC WITH CI RECYCLE

FIGURE 4. CATALYST DEACTIVATION TRENDS

CLOSE COUPLED BITUMINOUS (250)-AMOCAT IC
NONDEASHED BITUMINOUS (247) - SHELL 324
DEASHED BITUMINOUS (242, 243, 244) SHELL 324
TEMPERATURE 720°F

$K=2.63e^{-0.0134t}$

$K=2.02e^{-0.0134t}$ (ASSUMED)

$K=0.54e^{-0.00012t}$

$K=0.75e^{-0.00089t}$

$K=0.78e^{-0.00040t}$

$K=0.38e^{-0.00035t}$

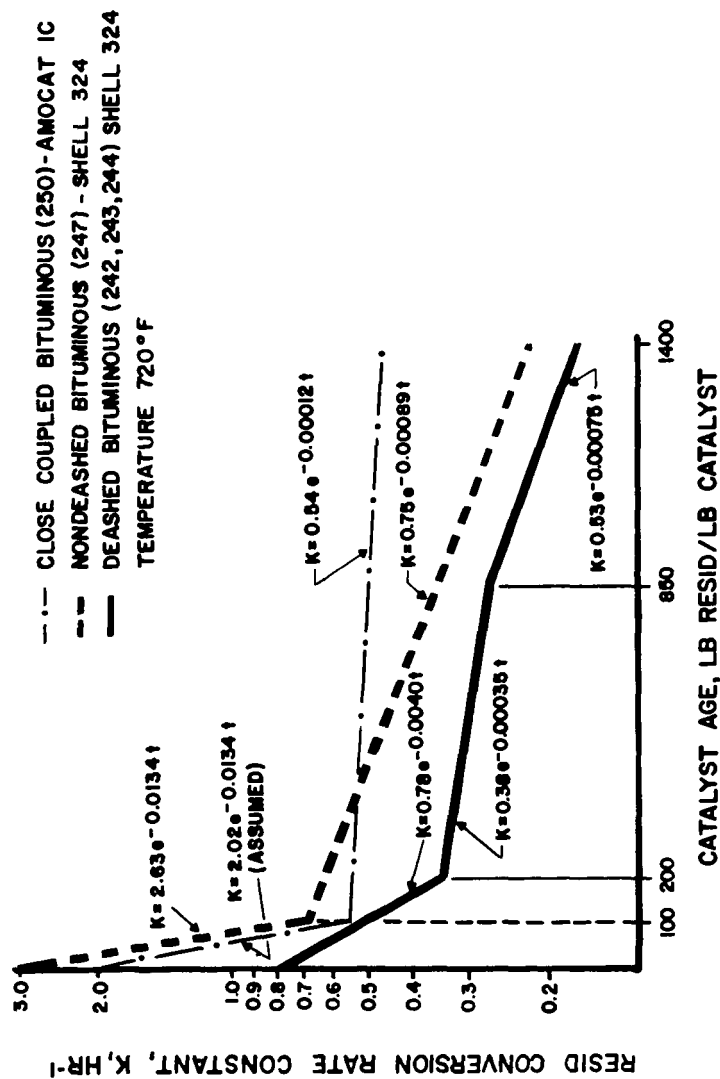$K=0.53e^{-0.00076t}$

RESID CONVERSION RATE CONSTANT, K, HR⁻¹
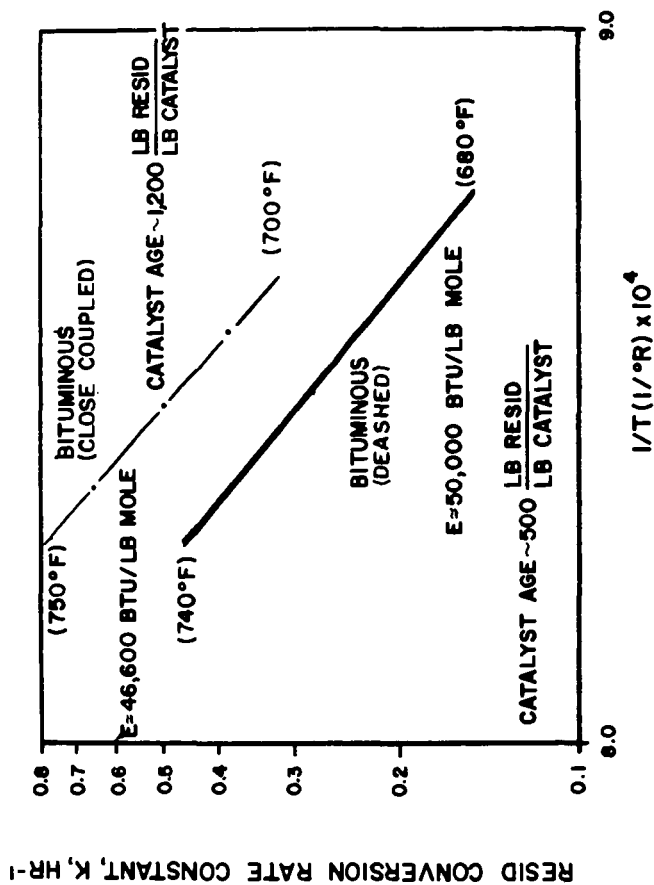
CATALYST AGE, LB RESID/LB CATALYST

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FIGURE 5. COMPARISON OF RESID CONVERSION RATE CONSTANTS

THE IMPACT OF THE CHEMICAL CONSTITUENTS OF HYDROTREATER FEED ON CATALYST ACTIVITY*

Frances V. Stohl and Howard P. Stephens
Sandia National Laboratories, Albuquerque, NM 87185

INTRODUCTION

The deposition of carbonaceous material on direct coal liquefaction catalysts is known to cause rapid and significant catalyst deactivation (1,2). Studies of hydrotreater catalyst samples from several different runs at the Wilsonville Advanced Coal Liquefaction R & D Facility have shown that greater than 75% of their hydrogenation activity and 50% of their hydrodesulfurization activity were lost within the first few days of coal processing (3). Hydrotreating light thermal resid from the third stage of the Kerr McGee critical solvent deasher yielded the least deactivation whereas hydrotreating the heavier nondeashed resid yielded the largest buildup of carbonaceous deposits and the greatest deactivation. These trends were due to differences in the compositions of the hydrotreater feeds. Previously reported work (4) has shown that carbonaceous deposits cause homogeneous poisoning of active sites and about a 50% decrease in the catalyst effective diffusivity, which is the diffusion coefficient within the extrudates.

As a result of the work on the Wilsonville catalysts, we have initiated a program to identify the hydrotreater feed components that are most detrimental to catalyst activity. Studies of the effect of hydrotreater feed boiling point cut on catalyst activity (5) have shown that processing a -550F component yields a 23% decrease in extrudate hydrogenation activity whereas hydrotreating an 850F+ component results in an 82% loss. Although hydrodesulfurization activity was not affected by the low boiling fraction, a 70% loss resulted from hydrotreating the highest boiling fraction.

In this paper we report the impacts on catalyst activity of four different chemical classes of compounds found in hydrotreater feeds. These chemical classes included the aliphatic hydrocarbons, neutral polycyclic aromatic compounds (PAC), nitrogen polycyclic aromatic compounds (N-PAC) and hydroxy polycyclic aromatic hydrocarbons (HPAH).

EXPERIMENTAL PROCEDURES

A hydrotreater process stream obtained from the Wilsonville facility and four classes of chemical compounds separated from this stream were each catalytically hydrogenated in microreactors. The starting feeds and used catalysts from these experiments were then characterized and the catalysts were tested for hydrogenation activity.

Materials

The catalyst was Shell 324M with 12.4 wt% Mo and 2.8 wt% Ni on an alumina support in the form of extrudates measuring about 0.8 mm in diameter and 4 mm in length. Prior to use, the catalyst was presulfided with a 10 mol% H_2S in H_2 mixture at 400C and atmospheric pressure for two hours. The V-178 hydrotreater process stream used in this study was obtained from the Wilsonville facility's run 247, which processed Illinois #6 bituminous coal in the Reconfigured Integrated Two-Stage Liquefaction process configuration(6). The V-178 stream, identified by the number of the storage tank from which it was derived prior to entering the hydrotreater, is the light portion of the hydrotreater feed and comprises about 35 wt% of the total feed. Distillation of the V-178 showed that the initial boiling point was 400F and 96.1 wt% boiled below 850F (5).

The V-178 process stream was separated into four chemical classes by adsorption column chromatography using neutral aluminum oxide (7). A 10 g sample was dissolved in chloroform and adsorbed onto 50 g alumina, which was then dried and placed on top of 100 g alumina in a 22 mm id column. The aliphatic hydrocarbon fraction was eluted first using hexane, then the PAC using benzene, followed by the N-PAC using chloroform and the HPAH using 10% ethanol in tetrahydrofuran. Solvent was removed from each fraction by evaporation under vacuum.

Hydrotreating Experiments

Each chemical class and the V-178 process stream were hydrotreated with presulfided catalyst in 26 cc batch microreactors at 300C for 2 hours with a 1200 psig H_2 cold charge pressure. The microreactors were charged with 0.5 g feed, 0.17 g presulfided catalyst and 1.5 g hexadecane, which was added to provide adequate mixing in the reactors because of the small amounts of feed available. The aged catalysts were Soxhlet extracted with tetrahydrofuran prior to analysis or activity testing. Elemental analyses of the V-178 stream, the four fractions and the aged catalysts were performed using standard methods.

Activity Testing

Hydrogenation activities of fresh and aged catalysts were determined by measuring the rate of hydrogenation of pyrene to dihydropyrene (4) in 26 cc microreactors at 300C with 450 psig H cold charge pressure. Experiments with catalyst ground to -200 mesh and whole extrudates enabled determination of the losses of both intrinsic and extrudate activities respectively.

RESULTS AND DISCUSSION

Feed and Catalyst Compositions

The compositions of the V-178 stream and the amounts and compositions of the four separated chemical classes, given in Table 1, show that the V-178 contains significant amounts of aliphatic hydrocarbons and the PAC fraction, and only low concentrations of nitrogen and hydroxy compounds. The 95% total recovery for the four chemical classes is good for this type of

separation. The high quality of the separations of the aliphatic
hydrocarbons and PAC fraction is indicated by the much higher H/C
ratio of the aliphatic fraction (1.70) compared to the PAC
fraction (1.16) and the low concentrations of nitrogen and oxygen
in these two fractions. In contrast, the N-PAC and HPAH fractions
both have significant amounts of oxygen and nitrogen indicating
the presence of compounds that contain both heteroatoms or
possibly some overlap of the fractions.
     Results of analyses of the aged catalysts, given in Table 2,
show that catalytic hydrotreating of the aliphatic and PAC
fractions yielded lower carbon accumulations on the catalysts than
hydrotreating the V-178 or the N-PAC and HPAH fractions.
Likewise, the catalysts used to hydrotreat the N-PAC and HPAH
fractions have significantly higher accumulations of nitrogen than
the catalysts used to hydrotreat the aliphatics and the PAC
fractions. The 0.6 and 0.5 wt% accumulations resulting from our
two hour experiments are comparable to the levels (0.5 to 0.6 wt%)
observed on the first catalysts, with catalyst ages of about 20 lb
resid/lb catalyst, withdrawn from Wilsonville runs. These results
show that the nitrogen buildup on the catalyst under process
conditions must be very rapid.

Hydrogenation Activity

     The measured intrinsic activity losses (α) and the measured
remaining extrudate activities (F) are given in Table 3. A
quantitative mathematical expression, reported previously (8),
relates F to α and effective diffusivity. Use of this equation
enabled us to determine the catalyst effective diffusivities. The
catalysts used to hydrotreat the V-178 and the aliphatic
hydrocarbon and PAC fractions showed a 20% decrease in effective
diffusivity from the fresh catalyst value of 5×10^{-6}
$cm^2/sec/cm^3$, whereas those used to hydrotreat the HPAH and
N-PAC fractions had greater than a 50% decrease. Recalculating
the F values without these changes in effective diffusivity (i.e.
with fresh catalyst effective diffusivity) (Table 3) shows that
less than 10% of the loss of fresh extrudate activity is due to
the changes in effective diffusivity.
     The relationship between F (corrected for changes in effective
diffusivity) and α also enabled us to differentiate the two
limiting modes of deactivation -- homogeneous and shell-
progressive poisoning. A plot of F vs α for the results from the
hydrogenation activity testing of the V-178 and the four chemical
classes is shown in Figure 1. Since the α values increase more
rapidly than the F values, the dominant mode of deactivation for
these catalysts is homogeneous poisoning of active sites (9). As
can be seen in Figure 1, the aliphatic hydrocarbons and the PAC
fraction caused less deactivation than the V-178, whereas the
N-PAC and HPAH caused more deactivation. This trend in
deactivation is inversely correlated with the carbon contents of
the aged catalysts given in Table 2. The catalysts used to process
the aliphatics and the PAC fraction have lower carbon contents
than the catalyst used to hydrotreat the V-178, whereas the
catalysts used to hydrotreat the N-PAC and HPAH fractions have
higher carbon contents. Hydrotreating the N-PAC fraction yields
the greatest deactivation with about an 87% loss of extrudate
hydrogenation activity and 98% of the active sites poisoned.

CONCLUSIONS

Separation of a light hydrotreater process stream into four chemical classes has shown that about half of the stream is composed of aliphatic hydrocarbons. There are also small amounts of N-PAC and HPAH fractions. Hydrotreating each of these four fractions and the whole process stream with catalyst has shown that all four fractions cause deactivation. The greatest deactivation is due to the N-PAC fraction, although the HPAH fraction also yields greater deactivation than the whole process stream. The deactivation is caused primarily by active site poisoning, with a lesser amount due to a decrease in effective diffusivity.

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Table 1. Compositions of the V-178 stream and the four chemical classes in weight percents.

	Wt % of V-178	C	H	N	O	H/C
V-178		87.69	10.05	0.23	1.08	1.38
Aliphatic hydrocarbons	46	87.27	12.36	< 0.10	0.10	1.70
Neutral polycyclic aromatic compounds (PAC)	35	90.15	8.70	0.10	0.17	1.16
Nitrogen polycyclic aromatic compounds (N-PAC)	5	83.60	7.93	3.61	2.81	1.14
Hydroxy polycyclic aromatic compounds (HPAH)	9	78.18	8.25	1.13	9.44	1.27

Table 2. Analyses of aged catalysts from microreactor runs (reported as weight percents).

Catalyst	C	N
V-178 run	3.87	0.3
Aliphatic hydrocarbon run	2.36	0.1
PAC run	2.71	0.1
N-PAC run	4.53	0.6
HPAH run	5.02	0.5

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Table 3. Results of activity testing experiments
(for fresh catalyst F = 1.00, α = 0.0)

Reactor Feed	F measured	α measured	F*
V-178	0.44	0.72	0.52
Aliphatic hydrocarbons	0.72	0.39	0.78
PAC	0.59	0.58	0.64
N-PAC	0.05	0.98	0.13
HPAH	0.19	0.92	0.26

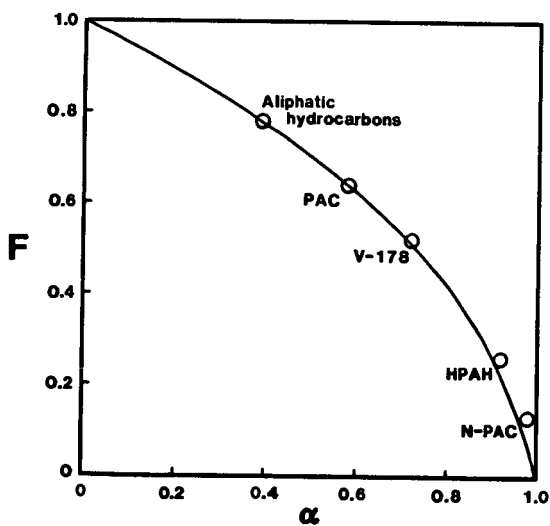* Corrected for changes in effective diffusivity.

Figure 1. F vs α plot for V-178 and the four chemical classes.

IMPROVEMENT IN COAL LIQUEFACTION SOLVENT QUALITY BY DEWAXING

R. A. Winschel, G. A. Robbins and F. P. Burke

CONOCO COAL RESEARCH DIVISION
4000 Brownsville Road
Library, PA 15129

ABSTRACT

Recycle oils from the Integrated Two-Stage Liquefaction (ITSL), H-Coal and Solvent Refined Coal (SRC) processes were dewaxed by variants of commercial dewaxing processes yielding up to 47 wt % "wax". Dewaxing methods used include the ketone and the urea adduction techniques. The clean waxes are reasonably pure paraffins. The dewaxed oils were substantially better coal liquefaction solvents than the original (non-dewaxed) oils in batch liquefaction tests. For example, in one case, dewaxing improved the conversion of a standard coal to tetrahydrofuran solubles at standard reaction conditions from 71% with the original oil to 87% with the dewaxed oil. These data provide a direct indication of the inimical effect of paraffinic components on solvent quality. The impact of solvent quality is particularly relevant to two-stage liquefaction, in which thermal first-stage reactions proceed in a recycle solvent. In addition, these results indicate the technical feasibility of dewaxing coal liquefaction recycle oils by commercially available technology to improve solvent quality and to produce a useful by-product. Dewaxing could be applied to any liquefaction process that uses a deashed (preferably distillate) recycle stream.

INTRODUCTION

Paraffinic and other saturated hydrocarbons are well known components of coal and coal liquefaction products (1). The presence of substantial quantities of saturated hydrocarbons in coal liquefaction recycle solvents has been reported (2). Increasing concentrations of these compounds (as well as of highly alkylated compounds) have been linked to a decreasing quality of the recycle oil as a donor solvent for coal liquefaction (2). Other work has demonstrated that the effectiveness of coal liquids as coal liquefaction donor solvents shows a negative correlation with the paraffinic nature of the coal liquid (3). In the development of the Consol Synthetic Fuels (CSF) (4) and Exxon Donor Solvent (EDS) (5) processes, it was recognized that the build-up of saturated hydrocarbons in the recycle solvent resulted in deteriorating solvent quality. Paraffinic and other saturated hydrocarbons are known to be non-donors (6) or at least very poor donors (7,8) at coal liquefaction conditions. Their presence in recycle oils reduces solvent quality, at least by diluting the active solvent molecules and at worst by acting as a detrimental antisolvent that leads to reduced solvent effectiveness.

Saturated hydrocarbons in coal liquefaction recycle oils are formed in part by complete hydrogenation of aromatics to form naphthenes. However, the majority of the paraffins (and particularly the n-paraffins) must ultimately arise either unchanged directly from the coal (9) or as products of the cracking of alkyl side-chains or of larger paraffins. If the recycle solvent is higher boiling than the major liquefaction products, saturates must exit the recycle loop by cracking to lighter products. Paraffins, however, tend to crack selectively to gases (5) thus consuming expensive hydrogen while producing undesirable gas.

The quality and paraffin content of the recycle solvent at equilibrium is fixed for each liquefaction process by the plant configuration, feed coal and operating conditions in use at any time. To reduce the paraffin content of the recycle solvent in order to improve its quality, operating conditions must be changed if the

feed coal and plant configuration are held constant. However, by changing operating conditions, product yield slate and/or product quality may be undesirably affected.

This paper presents a novel application of commonly used commercialized technology to improve the quality of coal liquefaction recycle solvents. That technology, in common use in the petroleum refining industry, is dewaxing. When applied to coal liquefaction recycle solvents, dewaxing improves donor solvent quality by removing predominantly the paraffins and other saturated hydrocarbons that are undesirable components. If applied commercially, a high-value by-product wax could be sold. For example, recent price ranges (10) of related products follow: paraffin wax, $0.16-0.46/lb; petrolatum, $0.30-0.40/lb; montan wax, $0.58-0.65/lb; micro-crystalline wax, $0.36-0.48 lb; and mineral oil, $2.68-3.10/gal. These prices are considerably greater than commanded by fuels. Removal of paraffins and other saturates from the liquefaction process this way may also reduce gas production and hydrogen consumption and would reduce the occurrance of wax precipitation at low temperature from products with boiling points similar to the dewaxed stream.

Various dewaxing methods are now, or have been, in commercial use in the petroleum industry (11) including pressing and sweating, centrifugation, solvent dewaxing (e.g., the propane and ketone processes) and urea adduction methods. The bulk of the experiments reported here used a laboratory version of the ketone process, though the urea adduction process was also tested, both with promising results. Commercially, methyl ethyl ketone is typically employed in the ketone process (11); acetone was used in our experiments for convenience. These experiments demonstrate on a small scale the technical feasibility of improving coal liquefaction solvent quality by dewaxing using commercially available technology.

The impact of solvent quality is particularly relevant to processes using a thermal reactor in which coal liquefaction proceeds in and depends upon a recycle solvent such as the ITSL, SRC-I, SRC-II and EDS processes. Dewaxing should be directly applicable to processes that recycle at least one distillate-only stream such as ITSL (the reconfigured mode in use at Wilsonville), SRC-I, EDS (without bottoms recycle) and H-Coal. It should also be possible to dewax any intermediate distillate stream if the recycle does not contain a separate distillate component. One experiment demonstrated that a deasphalted residual oil could also be dewaxed.

EXPERIMENTAL

Ketone Dewaxing

A weighed amount (about 85 g) of the oil to be dewaxed was mixed with acetone (Fisher HPLC grade) in the desired ratio (1/2 to 1/3.3 by volume) in a beaker equipped with a magnetic stirrer. All oils tested, except the single 850°F[+] resid, dissolved readily at room temperature. The contents were cooled while stirring in a dry ice/acetone bath to the desired temperature to precipitate the waxes. When the desired temperature (-20 or -50°C) was reached, the mixture was immediately filtered, while still cold, in a Buchner funnel equipped with a glass-fiber filter (Reeve Angel #934AH). The filter cake (wax) was washed with additional cold acetone approximately equaling the volume of the original oil/acetone mixture. This filtrate was set aside. The wax cake was washed through the filter with freshly distilled tetrahydrofuran (THF). Each filtrate (acetone and THF) was rotary evaporated at about 60°C to constant weight to remove all traces of solvents, leaving the dewaxed oil and the waxes, respectively, which were then weighed and analyzed. The product waxes were usually a white solid though some of the less pure waxes were discolored.

One sample, a solid deasphalted 850°F[+] resid, was ketone dewaxed using a somewhat different method. The solid (32g) was dissolved in 120g of an 80/20 v/v solution of acetone and freshly distilled toluene, then dewaxed as above at -50°C. These

waxes (12% of oil) were very impure and so were subjected to a second dewaxing procedure similar to the first except that the solvent used was 100 mL of a 70/30 v/v mixture of acetone and toluene. This product was a very hard brown waxy solid.

Urea Dewaxing

One oil sample was dewaxed by the urea adduction method. About 50g of the oil was weighed and diluted with an equal weight of CH_2Cl_2 (MCB reagent). To this mixture was slowly added about 50 mls of an aqueous solution of urea (Fisher certified) saturated at 80°C which crystallized upon cooling on contact with the oil/CH_2Cl_2 solution. The mixture was stirred for one hour, filtered in a Buchner funnel equipped with a glass-fiber filter, then washed with several aliquots of CH_2Cl_2. This filtrate was set aside. The filter-cake was washed with warm water to dissolve the urea leaving the waxes on the filter. The water wash was discarded. The waxes were washed through the filter with freshly distilled THF. The CH_2Cl_2 and THF filtrates were stripped of solvent by rotary evaporation to produce the dewaxed oil and the waxes, respectively, which were weighed and analyzed. The product wax was a white solid.

Solvent Quality (Microautoclave) Tests

Samples were tested for their effectiveness as coal liquefaction donor solvents using a standard microautoclave test. This test, called the modified equilibrium test, has been described in detail previously (3). Briefly, 6g of a standard coal and 9g of the sample to be tested are heated to 750°F for 30 min without added gas in a 30 mL microautoclave. The contents are cooled and extracted with THF to determine the conversion of coal to solubles. This test is an authentic coal liquefaction experiment. Solvent effects can be tested easily because there is no interfering catalyst or extraneous gas present. The results of this test serve as an empirical measure of donor solvent quality. Coal conversions obtained with several pure model compounds follow: n-tetradecane, 25.4%, 1-methylnaphthalene, 48.2%, tetralin, 85.4%. This test is reproducible to 1.2% absolute (standard deviation).

Other Analyses

Samples were analyzed by [1]H-NMR using a procedure described in detail elsewhere (3) to determine the effectiveness of dewaxing and to determine the purity of the waxes. Briefly, the [1]H-NMR spectrum is divided in regions roughly corresponding to different proton types. For example, the region between 10.0 and 4.7 ppm is assigned to aromatic protons and the region between 1.4 and 0.5 ppm is assigned to to paraffinic protons. Paraffinic protons are protons on internal $-CH_2-$ groups or $-CH_3$ groups of paraffins and long alkyl chains. Reproducibility is 0.2% absolute (standard deviation).

Gas chromatography (GC) was performed with a Perkin-Elmer Sigma 2000 instrument equipped with dual flame ionization detectors. The column, a 30m x 0.25mm DB-5 column from J&W Scientific, was initially at 50°C for 4 min, then programmed to 280°C at 4°C/min and held for 20 min. Carrier gas was 20 psig H_2. Injector and detector temperatures were 300°C. A split injection of 0.2μL of sample (0.1g/mL in THF) was used. Quantitation was based on peak areas referred to an n-decane internal standard.

Elemental analyses (C, H, N and S) were performed with Leco CHN-600 and SC32 instruments. Though these instruments were designed for the analysis of coals, not oils, reliable N and S determinations can be made. C and H values are less reliable, but are probably accurate to ±1% absolute.

Feed Oils

All samples were authentic coal liquefaction recycle oils.

#1   ITSL subbituminous distillate - A composite of the 850°F⁻ distillate portions of twenty daily samples taken between 5/6 and 8/6/84 of the recycle solvent (V-131B) from Wilsonville Run 246 made with Wyoming (Clovis Point mine) subbituminous coal.

#2   ITSL subbituminous distillate - The 850°F⁻ distillate portion of a sample of hydrotreater flashed bottoms (V-1067) taken 9/14/85 from Wilsonville Run 249 made with Wyoming (Clovis Point mine) subbituminous coal.

#3   ITSL bituminous distillate - A composite of the 850°F⁻ distillate portions of fourteen daily samples taken between 9/12 and 12/9/84 of the recycle solvent (V-131B) from Wilsonville Run 247 made with Illinois 6 (Burning Star mine) bituminous coal.

#4   H-Coal subbituminous distillate - the 1000°F⁻ distillate portion (96.1%) of a composite of seventeen daily samples taken between 9/1 and 9/17/80 of the "clean oil" (a component of the recycle solvent) from H-Coal PDU Run 10 made with Wyoming (Wyodak mine) subbituminous coal.

#5   SRC-1 bituminous distillate - the 1000°F⁻ distillate portion (95.6%) of a sample of recycle solvent taken 10/2/78 from Wilsonville Run 149 made with Kentucky #9 bituminous coal.

#6   ITSL subbituminous deasphalted resid - the hexane-solubles of a composite of the 850°F⁺ resid portions of twenty-one daily samples taken between 5/6 and 8/6/84 of the recycle solvent (V-131B) from Wilsonville Run 246 made with Wyoming (Clovis Point mine) subbituminous coal.

DISCUSSION

Results from dewaxing experiments using authentic coal liquefaction recycle oils are discussed below. In this report, "wax" refers to the precipitated portion of the oil obtained in the procedure, "dewaxed oil" refers to the non-precipitated portion and "feed oil" refers to the original, untreated oil. It should be recognized that the ketone process as commercially practiced is performed in two stages called dewaxing and de-oiling (11). Except in one case, these experiments were done in a single stage. Therefore, it is expected that these results could be further improved.

Experimental conditions and yields are shown in Table 1. Results of microautoclave liquefaction tests are shown in Table 2. Analyses of the various oils are shown in Table 3. ^{1}H-NMR spectra and gas chromatograms of the feed oil, dewaxed oil and waxes from experiment 5 are shown in Figures 1 and 2.

Wax Yields

Wax yields ranged from 3 to 47 wt % (Table 1). Wax purity spanned a range as well. Generally, the greatest yields of wax and the purest waxes were produced from oils derived from subbituminous coal (feed oils #1, 2 and 4). Those oils were very paraffinic, as determined by the paraffinic hydrogen content from ^{1}H-NMR and by GC (Table 3) and would be expected to produce the most wax. This is consistent with the concept that lower rank coals tend to be more paraffinic. One highly paraffinic oil produced from subbituminous coal (feed oil #2) yielded 47% of a reasonably pure wax (Tables 1 and 3).

The wax yields obtained in these experiments would not be expected to be attained at equilibrium in a liquefaction process employing dewaxing. The liquefaction processes from which these samples were taken all employed recycle and therefore, the total feed to these liquefaction processes included varying amounts of wax components. If dewaxing of all or part of the recycle were used, the wax content of the feed would be reduced thereby reducing the wax content of the product. It may be possible to dewax only that portion of the recycle solvent that is necessary

to keep wax levels below some set point. Dewaxing only a portion of the recycle solvent could reduce both capital and operating costs of the dewaxing unit.

Improvement in Donor Solvent Quality

In all cases, donor solvent quality, as measured by microautoclave tests, increased upon dewaxing. In general, the improvement in solvent quality upon dewaxing, as measured by the difference in the microautoclave tests with the feed oil and the corresponding dewaxed oil, increased with increasing wax yield. Thus, only 3% wax was removed in experiment 11 giving an improvement in donor solvent quality from 63 to 66%, whereas 47% wax was removed in experiment 14 giving an improvement in donor solvent quality from 71 to 87%. Clearly, the increase in donor solvent quality results from reducing the concentration of paraffins and other saturates which are non-donors and are generally considered to be poor physical solvents for coal liquids. In fact, paraffins have been found to be inimical to solvent quality in both microautoclave tests (3) and in the development of the CSF (4) and EDS (5) processes.

In direct coal liquefaction processes, the quality of the recycle oil generally is fixed by the feed coal, the operating conditions and the characteristics of the process. Making changes in operating conditions to improve the product slate or to compensate for catalyst deactivation can have the undesirable side effect of reducing solvent quality which, in turn, can affect product yields unexpectedly. Alternately, operating conditions that provide a high quality recycle solvent may not be desirable from a product yield or product quality standpoint. Dewaxing provides a means of improving recycle solvent quality that is independent of liquefaction conditions and may permit simultaneous optimization of product and recycle-solvent qualities.

It is interesting to note that the three dewaxed distillate ITSL recycle solvents all gave similar coal conversions in the microautoclave tests, even though the non-dewaxed feed oils gave significantly different results as shown below.

		Coal Conversion, wt % MAF	
Run No.	Feed Oil	Feed	Dewaxed
5	#1	80.9	88.2
13	#3	79.2	86.2
14	#2	70.8	87.1

This result would indicate that not only can donor solvent quality of recycle oils be improved by dewaxing, but that donor solvent quality can also be made more constant regardless of feed coal.

Effect of Temperature on Ketone Dewaxing

Experiments were performed with three feed oils at both -20 and -50°C. In each case, the lower temperature produced about twice as much wax (Table 1). The dewaxed oils produced at -50°C were better coal liquefaction donor solvents as measured by microautoclave tests (Table 2). This is consistent with the lower paraffinic content of those dewaxed oils (Table 3). However, the waxes produced at -50°C were lower purity paraffins than those produced at -20°C as evidenced by the increased aromaticities and carbon contents and decreased hydrogen and paraffinic hydrogen contents and by the GC results (Table 3). Even though the additional material removed at -50°C was largely not paraffinic, its removal further improved donor solvent quality. It is believed that the additional material removed at -50°C largely consists of highly saturated and alkylated compounds. Clearly, ketone dewaxing can be performed to maximize the improvement in solvent quality or to maximize the purity of the product wax depending on operating temperature. It should be possible to optimize both features simultaneously by selecting appropriate

temperature, time and solvent power conditions. These experiments were all operated with no hold time at temperature. Commercial petroleum dewaxing operations tailor solvent power by using solutions of varying ratios of ketone and toluene as the dewaxing solvent (11). Commercial petroleum operations also improve the selectivity of the process by operating in two stages in which the wax is separated and then de-oiled (11).

Ketone Dewaxing of Resid

One deasphalted 850°F$^+$ resid sample was dewaxed (experiment 12) yielding 7.9% of a very hard wax. The results of ^{1}H-NMR and elemental analyses (Table 3) indicate the wax is reasonably pure paraffin. This wax was too high boiling for complete GC analysis, but the eluted components were predominantly n-paraffins containing 24 to over 40 carbon atoms. This wax was very hard and had a freezing point upon cooling of 54°C by differential scanning calorimetry. This experiment showed that deasphalted resids can be dewaxed and may indicate that full-range coal lique-faction recycle oils can be dewaxed providing that they are solids-free and asphaltene-free. This may have applicability in ITSL and the developing Catalytic Two-Stage Liquefaction process in which the full-range recycle oil is typically solids-free and, when processing subbituminous coal, contains relatively low levels of asphaltenes (12,13).

Nature and Quality of Product Waxes

The product waxes were predominantly saturated hydrocarbons. This is evidenced by their very low H-aromaticities (as low as 0.3% aromatic/total hydrogen) and their elemental analyses (Table 3). Specifically, these saturated hydrocarbons were mostly paraffins as shown by the high concentration of paraffinic protons from ^{1}H-NMR analysis (as high as 91% paraffinic/total hydrogen). Even pure paraffins do not give 100% paraffinic protons in this ^{1}H-NMR analysis because of spinning side bands. For example, pure n-tetracosane gives 92.1% paraffinic protons in this analysis. n-Paraffins predominate in the gas chromatograms of the waxes (Table 3 and Figure 3), accounting for as much as 60% of the wax. The carbon preference indices (14) of the waxes were near unity, averaging 1.03 with a standard deviation of 0.04 (range = 0.92 to 1.09).

Dewaxing is most efficient for the higher molecular weight n-paraffins as seen by the GC data in Table 3. For all but one experiment, the n-paraffin of greatest concentration has the highest carbon number in the wax and the lowest carbon number in the dewaxed oil.

Enough wax was produced in experiments 13 and 14 to test the effectiveness of the wax as a donor solvent. The waxes from these experiments were also two of the least pure waxes recovered. As shown in Table 2, these waxes performed considerably more poorly than the corresponding feed oils, though not as poorly as pure n-tetracosane which gave 25.4% coal conversion in the same test. It is expected that the purer waxes would behave more similarly to the n-tetracosane.

ACKNOWLEDGEMENT

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TABLE 1

EXPERIMENTAL CONDITIONS AND PRODUCT YIELDS

Experiment No.	Feed Oil I.D.	Conditions		Yields, wt %		
		T, °C	Acetone/ Oil, v/v	Wax	Dewaxed Oil	Mass Balance
Urea Adduction Method						
2	#1	Room	(b)	5.0	88.8	93.8
Ketone Method						
4	#1	-20	2.0	9.1	90.7	99.8
5	#1	-50	3.3	20.6	79.3	99.9
14	#2	-50	3.0	47.4	52.0	99.4
7	#3	-20	3.0	14.5	83.2	97.7
13	#3(a)	-50	3.0	32.7	66.5	99.1
9	#4	-20	3.0	5.2	93.9	99.1
10	#4	-50	3.0	9.2	90.0	99.1
11	#5	-50	3.0	3.2	96.3	99.5
12	#6	-50	(c)	7.9	90.7	98.6

(a) Redistilled to 1000°F⁻ immediately before experiment (98.3% distillate).
(b) Urea method used, see Experimental section.
(c) 850°F⁺ residual oil used as feed, see Experimental section.

TABLE 2

MICROAUTOCLAVE TEST RESULTS

Experiment No.	Coal Conversion, wt % MAF		
	Feed Oil	Dewaxed Oil	Waxes
2	80.9	84.9	-
4	80.9	87.1	-
5	80.9	88.2	-
14	70.8	87.1	55.1
7	80.1	83.7	-
13	79.2	86.2	62.5
9	55.7	55.4/57.2	-
10	55.7	60.5	-
11	63.3	65.6	-

TABLE 3

ANALYSES OF FEEDS AND PRODUCTS

Experiment No.	Fraction	Hydrogen Types by ^{1}H-NMR, % Aromatic	Paraffinic	Elemental Analysis, wt % (a) C	H	N	S	Conc., wt %	n-Paraffins by GC C #'s Observed Range	Max. Conc.
2	Feed	14.6	42.6	89.1	10.0	0.3	<0.1	5.7	15-33	22
	Dewaxed	17.0	34.2	88.4	9.8	0.4	<0.1	3.2	15-32	22
	Wax	2.6	82.5	80.9	13.9	0.9	<0.1	47.7	13-35	25
4	Feed	14.6	42.6	89.1	10.0	0.3	<0.1	5.7	15-33	22
	Dewaxed	19.5	32.5	88.4	9.9	0.4	<0.1	1.7	15-24	17
	Wax	2.2	88.4	84.7	14.6	0.1	<0.1	51.4	15-35	25
5	Feed	14.6	42.6	89.1	10.0	0.3	<0.1	5.7	15-33	22
	Dewaxed	19.3	28.8	89.4	9.1	0.3	<0.1	0.5	15-28	18
	Wax	2.7	71.2	87.0	12.8	0.3	<0.1	29.2	13-35	25
14	Feed	9.3	49.4	87.9	11.0	0.3	<0.1	6.2	15-34	26
	Dewaxed	15.3	33.6	89.4	10.2	0.4	<0.1	1.0	15-23	17
	Wax	4.1	62.0	87.4	12.7	0.2	<0.1	15.9	15-34	26
7	Feed	10.8	40.7	88.5	10.2	0.2	<0.1	2.3	15-31	20
	Dewaxed	12.5	38.4	88.9	10.0	0.2	<0.1	1.2	15-28	19
	Wax	4.6	57.6	87.6	11.9	0.1	<0.1	11.8	15-35	25
13	Feed	10.8	42.5	88.4	10.8	0.2	<0.1	1.9	15-31	20
	Dewaxed	14.1	35.2	89.1	10.2	0.3	<0.1	0.6	15-24	17
	Wax	5.0	55.4	88.0	12.4	0.2	<0.1	5.5	15-32	23
9	Feed	21.3	40.3	88.9	10.3	0.4	<0.1	6.2	16-31	16
	Dewaxed	22.9	35.6	88.6	10.3	0.4	<0.1	3.5	16-23	17
	Wax	0.3	91.3	84.7	15.3	0.1	<0.1	58.9	14-33	19
10	Feed	21.3	40.3	88.9	10.3	0.4	<0.1	6.2	16-31	16
	Dewaxed	24.6	32.5	88.6	9.8	0.5	<0.1	2.3	14-24	15
	Wax	1.9	90.9	84.4	15.4	0.1	<0.1	60.1	14-35	16
11	Feed	25.9	31.4	86.6	9.5	0.8	0.3	2.8	15-30	15
	Dewaxed	26.9	30.1	86.4	9.3	0.8	0.3	0.9	15-24	15
	Wax	0.8	86.7	84.6	14.5	0.1	<0.1	53.1	12-36	17
12	Feed	20.7	33.8	90.0	8.5	0.6	<0.1	-	-	-
	Dewaxed	23.8	26.4	90.2	8.0	0.4	<0.1	-	-	-
	Wax	2.8	76.9	87.0	12.7	0.4	<0.1	-	24->40	-

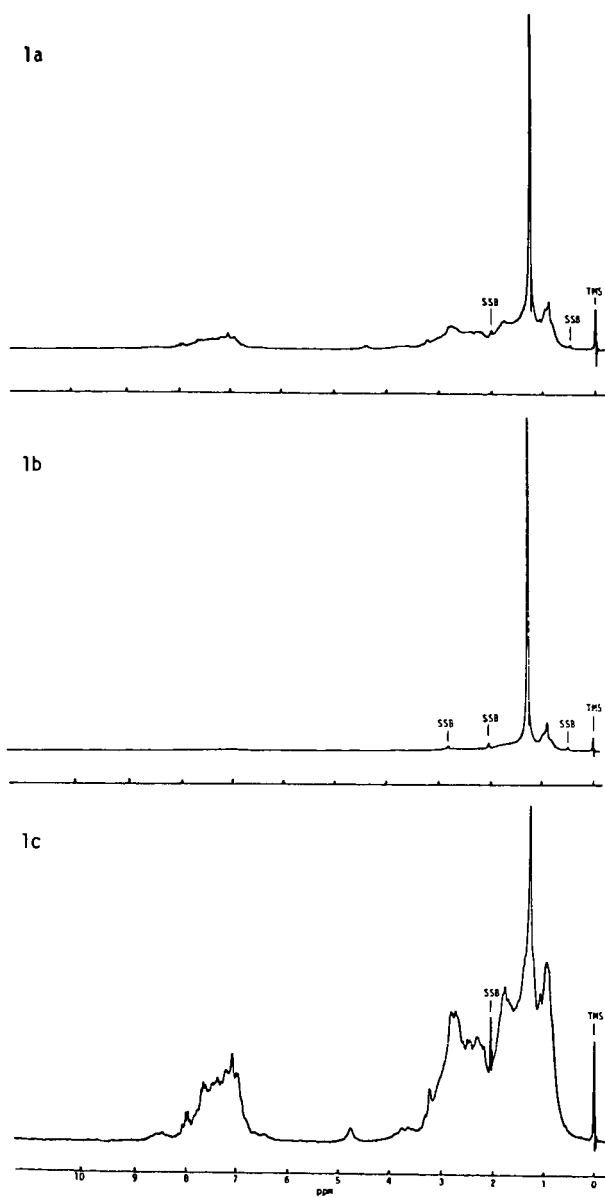(a) carbon and hydrogen values probably only accurate to ±1% absolute.

Figure 1. ¹H-NMR spectra of samples from experiment 5. (a) feed oil, (b) wax, (c) dewaxed oil. TMS – tetramethylsilane internal reference, SSB – spinning side band.
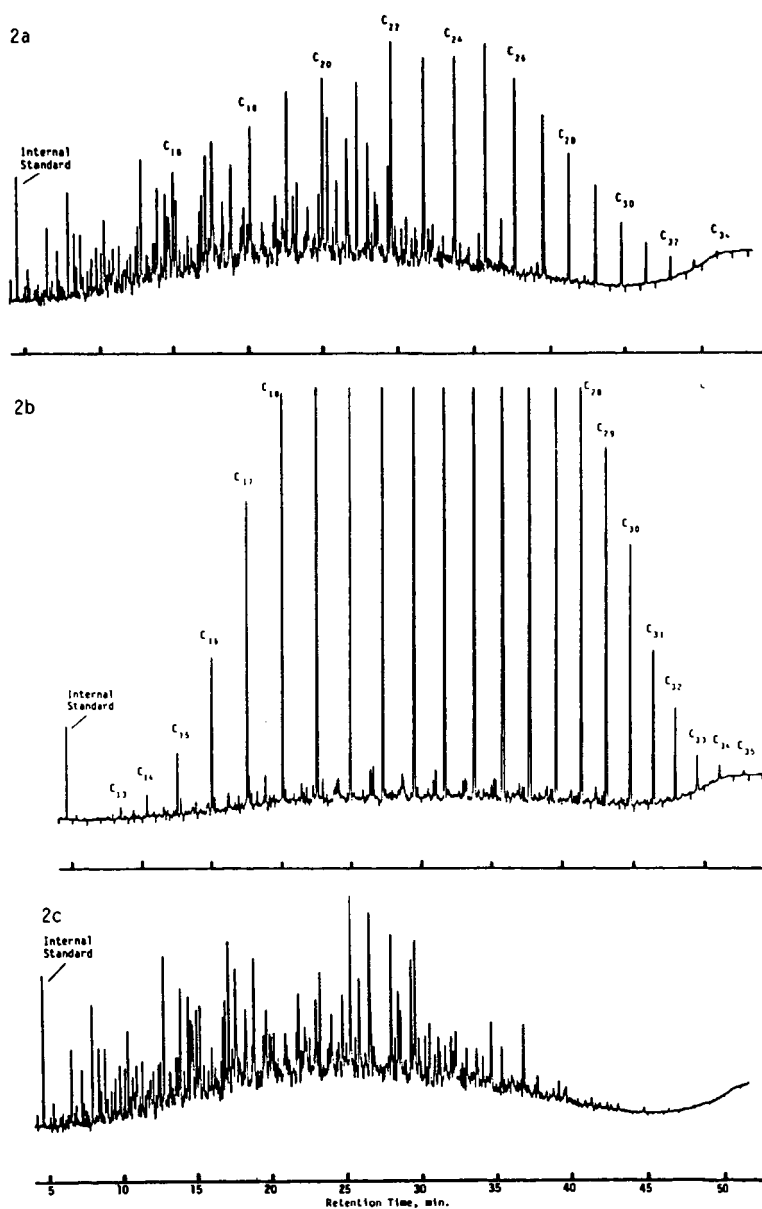
Figure 2. Gas chromatograms of samples from experiment 5. (a) feed oil, (b) wax, (c) dewaxed oil. (internal standard, n-decane)

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PERFORMANCE OF THE LOW TEMPERATURE FIRST STAGE OF HRI'S CATALYTIC TWO-STAGE LIQUEFACTION PROCESS

J. B. McLean, A. G. Comolli and T. O. Smith

Hydrocarbon Research, Inc.
(A Subsidiary of Dynalectron Corporation)
P. O. Box 6047
Lawrenceville, New Jersey 08648

ABSTRACT

Hydrocarbon Research, Inc. (HRI), under the sponsorship of the U. S. Department of Energy (DOE), is developing a catalytic two-stage coal liquefaction process. The process consists of two direct-coupled ebullated-bed reactors in series, with the first stage operated at lower temperatures (<800°F) than typically used in direct liquefaction. Studies of both bituminous and sub-bituminous coals in a nominal 50 lb/day continuous, integrated recycle bench unit have shown considerable improvements in both distillate yield and product quality over other processes. In order to better understand the chemistry of the unique first-stage reactor conditions, a special on-line sampling system was added to the bench unit. Samples obtained over a wide range of operating conditions indicate that the first stage is an efficient hydrogenation system, achieving balanced rates of coal conversion and dissolution, solvent to coal hydrogen transfer, solvent regeneration, and liquefaction product upgrading and stabilization. Differences in responses of the two coals studied are noted and discussed.

INTRODUCTION

Hydrocarbon Research, Inc. (HRI) has long been actively involved in the development of coal liquefaction process technology. The H-Coal® Process, featuring a single-stage ebullated-bed catalytic reactor, was successfully developed and demonstrated through operation of a 200 ton per day pilot plant at Catlettsburg, Kentucky, in the early 1980's.[1]   In 1981-1982, HRI conducted a series of laboratory investigations to evaluate various two-stage liquefaction concepts which featured a thermal first-stage reactor followed by a closely coupled, ebullated bed, catalytic second stage.[2-6] The results of these programs formed the basis for the current Catalytic Two-Stage Liquefaction (CTSL) concept, which features two direct-coupled, ebullated-bed reactors in series. Under DOE sponsorship, HRI has been conducting a development program for the CTSL Process since 1983. Program results have been reported[7-11] with C4-975°F distillate yields of 65 W % MAF coal achieved for both Illinois No. 6 and Wyodak coals. The process economics have been shown to be favorable in comparison with other two-stage approaches by an independent contractor's study[12] for both coals.

PROCESS FEATURES

The salient features of the CTSL Process are listed in Table 1. The key feature which distinguishes this from other single- or two-stage processes is the operation of a low temperature (<800°F) first-stage liquefaction reactor which contains an effective hydrogenation catalyst. Here, coal is converted by dissolution in the recycle solvent at a controlled rate, allowing the catalytic hydrogenation reactions important for solvent regeneration and liquefaction product stabilization to keep pace with the rate of coal conversion. The second stage, operating at conditions more similar to the single stage H-Coal® Process (but still less severe), finishes the job of coal conversion while converting primary liquefaction products to high quality distillates. Overall, the process produces higher yields of better quality distillate products than competing technologies.

It is generally recognized that coal conversion to liquids is a thermal process (involving hydrogen transfer from donor compounds in the recycle solvent), and that the function of a catalyst in a direct liquefaction system is to hydrogenate the solvent to provide those donor compounds, as well as to upgrade the thermal liquefaction products. As a result, two-stage liquefaction concepts were developed which featured a thermal first-stage liquefaction reactor, followed by a catalytic second stage for solvent hydrogenation and product upgrading. These are represented by the Integrated Two Stage Liquefaction (ITSL) processes developed at Lummus-Crest[13] and the Wilsonville Advanced Coal Liquefaction Pilot Plant,[14] and the Direct Coupled Two-Stage Liquefaction system (DC-TSL) developed at HRI. These processes rely on production of a high quality recycle donor solvent, produced at low (<800°F) catalytic stage temperatures which favor hydrogenation over cracking. One primary drawback to this sequential approach is that solvent donor compounds are depleted in the non-catalytic liquefaction reactor, so that the final "spent" solvent quality is much poorer than the inlet recycle solvent. Also, the lack of catalytic product stabilization leads to undesirable regressive recombination reactions at the conditions necessary to achieve complete coal conversion.

The CTSL Process avoids these drawbacks by conducting liquefaction at a much slower rate in the low-temperature first stage. The first stage conditions provide a very efficient hydrogenation atmosphere so that hydrogen shuttling compounds in the solvent can be effectively regenerated and reused over and over again. Thus the solvent does not become "spent". Primary liquefaction products are also efficiently hydrogenated as they are formed, reducing the tendency for regressive reactions. By conducting conversion and hydrogenation functions simultaneously rather than sequentially, the "lifetime" of unstable thermal products is reduced. The second stage then completes the coal conversion at more typical liquefaction temperatures in the presence of a much higher relative concentration of high quality solvent. Second-stage conditions are chosen to optimize coal and residuum conversion and heteroatom removal, without approaching a thermal severity where dehydrogenation of first-stage products become significant. This paper presents data to support each of the first-stage functions listed in Table 1, which in turn provide the basis for the observed overall performance benefits of the two-stage concept.

BENCH UNIT DESCRIPTION

Process development studies have been conducted in HRI's continuous two-stage Bench Unit 227, shown in Figure 1. It is necessary to study the process in a continuous unit with self-sustained recycle solvent generation in order to fully understand the results and avoid the pitfalls of smaller batch or once-through experimental units. The unit features two 2000cc ebullated-bed reactors in series. A special high-pressure, on-line sampling system was adapted to the first-stage reactor to obtain the data required to independently assess the effectiveness of the two reactor stages. Prior to this, it was necessary to attempt to interpret the effects of first-stage variables based on overall results only. Since the reactors are direct-coupled, and the desired sample quantities represent a significant fraction of the first-stage reactor inventory, the design and operation of the sampling system is critical to obtain representative samples while minimizing unit disruption. The data presented in this paper are based on analyses of the first-stage samples. A continuous atmospheric still was also added to the unit during this program to provide accurate control of recycle solvent cut points. The atmospheric still bottoms are subjected to further batch filtration and/or vacuum distillation operations to study various recycle oil preparation techniques. System inventories are minimized in order to provide a rapid lineout response to condition changes.

PROGRAM HISTORY

A summary of bench unit operations conducted through February 1986 is shown in Table 2. The first year of the program was dedicated to Illinois No. 6 coal, and the second year to Wyodak sub-bituminous coal. Following renewal of the contract for two additional years in 1985, additional studies are being conducted with Illinois No. 6 coal. Each of these coals has been studied in previous single- and two-stage operations, so that an extensive data base for comparison of CTSL results exists. The implementation of the first-stage sampling system, late in the original Illinois coal program, greatly enhanced the understanding of the observed favorable performance, and first-stage sample analyses were used extensively in all subsequent work.

FIRST-STAGE PERFORMANCE

Coal Conversion Rate

One of the primary benefits of the lower temperature liquefaction stage is that coal is converted at a controlled rate, allowing a balance between thermal and catalytic reaction rates to be maintained. Figures 2 and 3 show the relationship between coal conversion (to quinoline solubles) and both temperature and residence time for several sets of data for both coals. In each case, the connected data points represent studies where all other parameters (second-stage conditions, solvent/coal ratio, etc.) are held constant. Comparisons of non-connected points should not be made since other parameters are different as well. Note that increasing severity by both parameters always results in an increased coal conversion, indicating kinetic rate control. It should also be noted that

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overall process conversions were in all cases substantially higher, and tended to correlate with first-stage conversions. In the case of the Illinois No. 6 coal, it appears that "maximum" coal conversions (95-96%, typically) are being approached at 750-775°F, while the Wyodak coal is much slower to convert and requires additional thermal severity (90-93% conversion typically achieved in second stage).

Hydrogen Transfer Efficiency

Figure 4 shows the atomic hydrogen/carbon ratio of THF insoluble IOM from both first- and second-stage samples as a function of coal conversion for Wyodak coal. Surprisingly, this ratio stays quite high (at or above the original coal level) over a wide range of first-stage conversions. It would be expected that the most reactive components of the coal would be the most hydrogen-rich, and would leave behind a residue of depleted hydrogen content. This in fact does occur in higher temperature, thermal processes. However, the controlled conversion rate in CTSL allows for efficient hydrogen transfer to the coal as it reacts. A similar relationship has been noted for the Illinois No. 6 coal. Only at the more severe thermal conditions of the second stage does the hydrogen transfer appear to drop off, as evidenced by the lower H/C ratios for the high conversion samples.

No attempt has been made here to distinguish "unreacted coal" from IOM formed by regressive reaction. However, the combination of the observed kinetic response, residue analyses, and mild severity conditions indicate that regressive reaction should be minimal in the first stage. While residue analyses are interesting, they are of limited utility, particularly since the overall coal conversions achieved in CTSL are no better than in the single-stage H-Coal® Process. Of more importance are the analyses of the liquids which are formed at first-stage conditions, which are substantially different than those produced in other direct liquefaction processes.

Solvent Hydrogentation

Since the coal is liquefied in the presence of a catalyst at conditions which favor hydrogenation, donor species present in the solvent can be regeneratively rehydrogenated. This is illustrated for a typical condition for each coal in Table 3, which compares properties of first-stage oil and pressure filter liquid (PFL), which is both the second-stage oil and process recycle solvent. Note that even though substantial coal conversion has occurred in the first stage in each case, there is no indication of solvent quality deterioration - in fact, the solvent quality, as measured by standard microautoclave tests, has improved. This is due to simultaneous solvent rehydrogenation, as indicated by the improved hydrogen content and lower aromatics level in the first-stage liquid. This is a key difference from other two-stage processes, where solvent quality is depleted in the liquefaction stage due to more severe thermal conditions and the lack of an effective hydrogenation catalyst. One positive benefit of this effect on the overall process is that the feed solvent/coal ratio can be set at a minimum pumpable level, without concern for available donor hydrogen levels. Bench unit operations on Illinois No. 6 coal have been conducted at feed slurry solvent/coal ratios as low as 1.1, and still lower ratios may well be possible on a larger scale. This has a large favorable impact on process economics.

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Recycle Residuum Hydrogenation

Residuum in the recycle solvent is upgraded by hydrogenation in the first stage, making it more reactive for cracking to lighter distillates in the second stage. This is indicated in Table 4, which shows net positive yields of residuum components in the first stage, and net conversion to distillates in the second stage. As a result, the overall 975°F+ yields are quite low, and the quality (as indicated by high oil and low preasphaltene contents) is also quite good.

Catalytic Stabilization/Upgrading of Primary Liquefaction Products

The discussion above had highlighted the effect of first-stage conditions on recycle solvent properties. In fact, the oil properties presented are for liquids which are a blend of recycle solvent and direct first-stage products. Depending on feed solvent/coal ratio and net first-stage reactions, the first-stage oil content is estimated to be 20-50% directly produced from coal, with the remainder derived from recycle solvent. (Of course, in an integrated operation all of the material is ultimately coal-derived; here the distinction is being made to specifically include material which has not yet been exposed to second-stage conditions.) With this in mind, the level of hydrogenation is even more notable since the primary liquefaction products should be of substantially lower quality than the recycle solvent.

COAL COMPARISON

Evidence has been presented for both Illinois No. 6 and Wyodak coals which support the process concept of first-stage hydrogenation, resulting in improved overall liquid yields and product qualities. However, the response of the two coals - and hence the optimum process conditions for each - are quite different. As has been noted in Figure 2, the sub-bituminous coal is much slower to convert, and probably requires a first-stage temperature of at least 750°F to achieve enough coal conversion for the catalytic treatment to be effective. The bituminous coal liquefies much more readily, but (as noted in Table 4) gives much higher net residuum yields. Work to date has indicated optimum performance at 750-775°F, but it is probable that this can be reduced by the appropriate combination of catalyst, space velocity, etc. This objective is being pursued in the present program. Other items being investigated include optimization of liquid yield distribution, particularly the extinction conversion of all 650°F+ products, and operation at lower second-stage temperatures to improve product quality and extend catalyst life.

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TABLE 1

HRI'S CATALYTIC TWO STAGE LIQUEFACTION PROCESS

FIRST STAGE

    "Low" Temperature (<800°F)
    Hydrogenation Catalyst (e.g. Amocat 1C, NiMo)

    Functions: Coal Conversion (controlled rate)
            Hydrogen Transfer to Reacting Coal
            Solvent Hydrogenation - Regenerative
            Recycle Residuum Hydrogenation
            Catalytic Stabilization/Upgrading of Primary Liquefaction Products

SECOND STAGE

    "High" Temperature (>800°F)
    Hydroconversion Catalyst (e.g. Amocat 1A, CoMo)

    Functions: Complete Coal Conversion (Thermal in an improved solvent environment)
            Residuum Conversion to Distillate Products
            Heteroatom Removal
            Avoid Dehydrogenation

OTHER PROCESS FEATURES

    Reaction Stages are Direct-Coupled
    Ebullated Bed Technology Scaleable Based on H-Coal®/H-Oil® Experience
    Highest Conversion to Distillates of any Direct Liquefaction Process
    More Aliphatic/Petroleum-Like Products than other Direct Liquefaction Processes
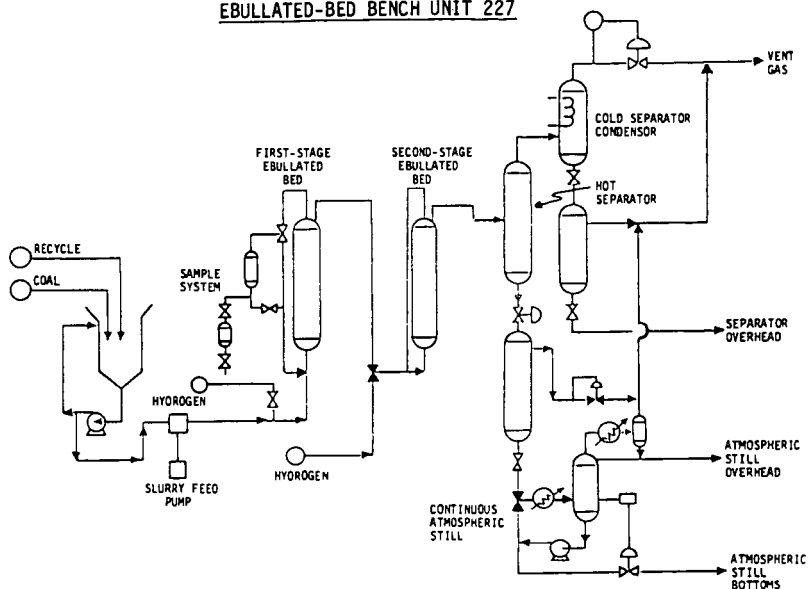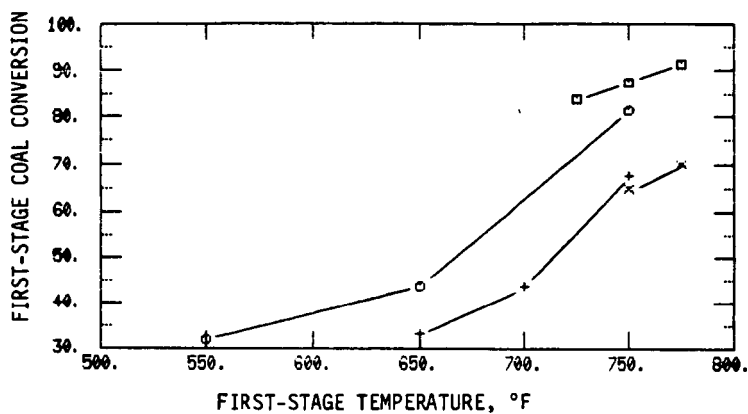
FIGURE 1

EBULLATED-BED BENCH UNIT 227

TABLE 2

CATALYTIC TWO STAGE LIQUEFACTION PROCESS DEVELOPMENT
History of Bench Unit Operations (through February 1986)

	Number of		Conditions	First Stage
	Runs	Days		Samples
Illinois No. 6 Coal (1983-1984)				
Process Variable Studies	8	149	38	-
First Stage Sampling	1	12	4	4
Process Demonstration	1	25	1	-
Total Illinois No. 6				
(1983-1984)	10	186	43	4
Wyodak Sub-bituminous Coal				
(1983-1985)				
Process Variable Studies	3	80	25	18
Process Demonstration	2	44	3	B
Total Wyodak Coal	5	124	28	26
Illinois No. 6 Coal (1985-1986)				
Process Variable Studies	2	57	16	15

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FIGURE 2

FIRST-STAGE COAL CONVERSION (W % MAF) VERSUS TEMPERATURE

o Illinois No. 6 (Run 227-18)
□ Illinois No. 6 (Run 227-32)
+ Wyodak, Run 227-22 (Conditions 4, 5 and 6)
x Wyodak, Run 227-22 (Conditions 7 and 9)

FIGURE 3

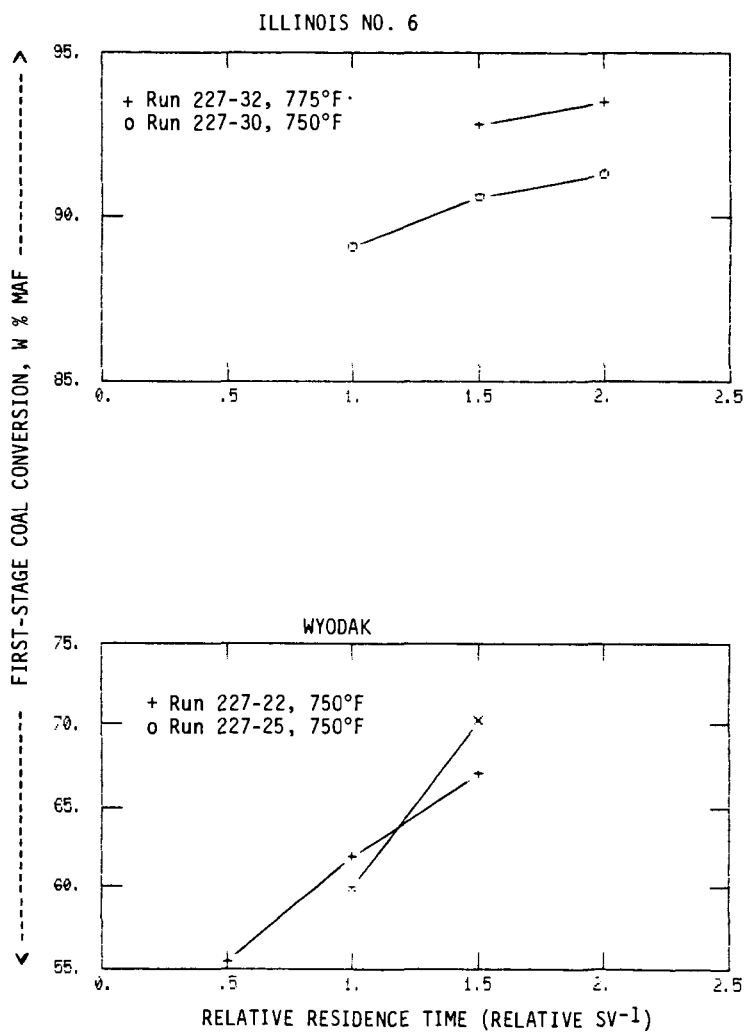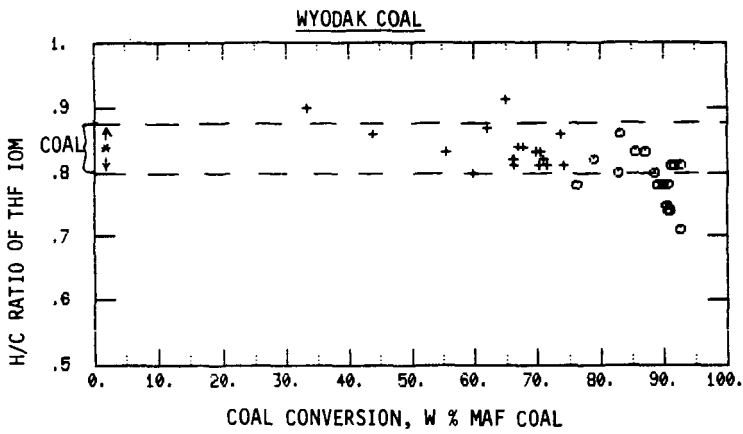## FIRST-STAGE COAL CONVERSION (W % MAF) VERSUS TIME

ILLINOIS NO. 6

+ Run 227-32, 775°F·
o Run 227-30, 750°F

WYODAK

+ Run 227-22, 750°F
o Run 227-25, 750°F

FIRST-STAGE COAL CONVERSION, W % MAF

RELATIVE RESIDENCE TIME (RELATIVE SV^{-1})

FIGURE 4

REACTOR SOLIDS HYDROGEN/CARBON ATOMIC RATIO
VERSUS COAL CONVERSION

WYODAK COAL

+ First-Stage Solids
o Second-Stage Solids
* Range of Analyses for Fresh Coal

TABLE 3

COMPARISON OF FIRST-STAGE OIL AND PFL PROPERTIES

	ILLINOIS NO. 6 COAL		WYODAK COAL	
	Run No. 227-18-12		Run No. 227-25-16	
	< ----------- S T A G E S ------------ >			
	FIRST OIL	SECOND PFL	FIRST OIL	SECOND PFL
Bench Unit Coal Conversion, W % MAF	87.1	92.7	73.6	91.6
Microautoclave Solvent Quality Test, W % THF Conversion				
HRI[1]	83.3	76.6	54.5	52.0
Conoco[2]*	82.9	79.9	64.5	64.0
H/C Ratio - 650-850°F	1.28	1.25	1.40	1.40
850-975°F	1.19	1.13	1.34	1.24
975°F+	0.95	0.91	1.06	0.98
Proton* NMR - % Aromatics				
850°F- Distillate	14.6	15.7	11.0	10.6
850°F+ Residuum	29.2	31.4	19.3	25.3

(1) HRI procedure uses matched coal and solvent.
(2) Conoco procedure uses Indiana V coal.
* Data provided by CONOCO.

TABLE 4

975°F+ RESIDUUM PROPERTIES

	ILLINOIS NO. 6		WYODAK	
	Run 227-32-9		Run 227-25-16	
	< ------- S T A G E S ------- >			
	First	Second	First	Second
W % 975°F+ In Oil	39.5	32.1	12.1	9.0
975°F+ Properties				
H/C Ratio	1.03	0.99	1.06	0.98
% Nitrogen	0.65	0.53	0.79	0.73
% Oil	64.5	71.9	75.3	84.7
% Asphaltenes	28.6	23.5	24.1	15.0
% Preasphaltenes	6.9	4.6	0.6	0.3
Estimated Net 975°F+ Yield - W % MAF Coal				
Oils	9.6	-3.2	2.4	-0.2
Asphaltenes	9.3	-7.2	2.2	-1.8
Pre-Asphaltenes	3.3	-2.9	0.1	-0.1
TOTAL	22.2	-13.3	4.7	-2.1

TRANSPORTATION FUELS FROM TWO-STAGE LIQUEFACTION PRODUCTS

Richard F. Sullivan

Chevron Research Company, P. O. Box 1627
Richmond, California 94802-0627

INTRODUCTION

For several years, Chevron Research Company under a contract with the US Department of Energy has been studying the refining of coal liquids. Detailed results are given in a series of DOE Interim Reports (1). The earlier work emphasized upgrading of products from single-stage processes: SRC-II, H-Coal, and EDS. More recently, we have been studying products from two different two-stage processes: the Integrated Two-Stage Liquefaction (ITSL) Process and the Catalytic Two-Stage Liquefaction (CTSL) Process.

The purpose of this paper is to compare results for syncrudes from single-stage and two-stage processes, from different two-stage processes, from different coals [Illinois No. 6 (bituminous) and Wyodak (subbituminous)], and of different boiling ranges from a given coal and process.

The ITSL process, developed by Cities Service and Lummus Crest, Inc., operates with a high temperature (over 800°F) first stage with no added catalyst. The product is then deashed, and sent to a second-stage that operates at lower temperatures (typically below 800°F) with an ebullated catalyst bed (2).

The CTSL process, developed by Hydrocarbon Research, Inc. (HRI), operates with two catalytic ebullated-bed stages. In contrast to the ITSL process, the CTSL first stage operates at a lower temperature (below 800°F) than the second (which operates above 800°F) (3).

Depending upon how each liquefaction process is operated, the end point (EP) of the net whole-liquid product will vary. Typically, part or all of the vacuum gas oil (VGO) made by the process is used as recycle solvent for the coal. Some or all of it is ultimately converted to lower boiling products. Thus, the net whole-liquid product can have an EP ranging from below 650°F to over 850°F. As we will see, the ease or difficulty of upgrading is affected to a large extent by product EP. The 650-850°F VGO is relatively difficult to upgrade, but is reported to be an excellent recycle solvent. Therefore, there may be both upstream and downstream advantages to recycling this VGO, as shown for example, by MacArthur et al (4). Ultimately, of course, the costs and yields of both liquefaction and upgrading must be used to determine the optimum EP.

In this paper, we will use results for upgrading products from the H-Coal process (1, 5) as our primary basis for comparison with single-stage processes.

FEEDSTOCKS

Key factors that determine how easy or difficult a particular syncrude is to refine are EP, boiling range, hydrogen content, and heteroatom content. Also, hot-heptane insoluble compounds (low-solubility polycyclic-aromatic and polar compounds, asphaltenes, and ash) can make syncrudes difficult to processes.

Table I shows properties of pairs of H-Coal and ITSL syncrudes
derived from Illinois coal. Table II shows properties of pairs of
H-Coal, CTSL, and ITSL syncrudes derived from Wyodak coal. In each
case, the syncrude identified as "A" had a higher EP than that
identified as "B". The A syncrudes were blended from components
supplied HRI and Lummus in ratios recommended by DOE to represent, as
nearly as possible, "net whole-liquid products" from these processes.
[Note: the heavy fractions of Illinois ITSL A and Wyodak CTSL A,
as-received, contained large quantities of hot-heptane insolubles and
metals that presumably would not be part of the commercial net
product. Therefore, the heavy fractions were redistilled to remove
these impurities before the syncrude blends were prepared.] The B
syncrudes were either fractions provided by DOE to represent product
from lower-cut-point operation (Illinois ITSL B, Wyodak CTSL B), or
redistilled from higher-boiling syncrudes (Illinois H-Coal B, Wyodak
H-Coal B, Wyodak ITSL B). [Note that part of the front end was
missing from the Wyodak ITSL oils.]

The distillation curves for the Illinois syncrudes are shown in
Figure 1. The contrast between the boiling ranges of H-Coal and ITSL
oils is quite striking. The H-Coal oil was quite low boiling--roughly
50% boiled below 400°F. The ITSL oil was considerably higher
boiling--less than 20% boiled below 400°F, 70-75% boiled between 400
and 700°F.

Table I
SYNCRUDES FROM ILLINOIS NO. 6 COAL

Process	<----H-Coal---->		<-----ITSL------->	
Sample Identification	A	B	A	B
LV% of As-Received Oil	100	87	95	69
Inspections				
Gravity, °API	25.8	28.1	13.6	17.6
Sulfur, ppm	2000	1400	865	700
Nitrogen, ppm	4600	3300	1050	730
Oxygen, ppm	18000	19600	2600	1800
Hydrogen, Wt %	11.29	11.44	10.19	10.68
Carbon, Wt %	86.25	86.13	89.35	88.99
Hot-Heptane Insolubles, ppm	3500	54	375	290
TBP Distillation, °F (ASTM D2887)				
St/5	56/177	56/170	97/275	97/214
10/30	213/333	200/310	375/532	314/471
50	404	380	602	560
70/90	476/588	440/508	665/745	609/676
95/99	654/765	538/589	793/859	703/763
Boiling Range, LV%				
St-400°F	49	57	12	18
400-700°F	48	43	69	76
700°F+	3	0	19	6

Process	<-----H-Coal--->		<-----CTSL------>		<-----ITSL----->	
Identification	A	B	A	B	A	B
LV% of As-Received Oil	100	96	93	62	100*	52*
Inspections						
Gravity, °API	35.1	35.1	29.0	36.1	8.8	15.8
Sulfur, ppm	410	250	140	88	580	305
Nitrogen, ppm	1700	1500	1230	935	1670	1020
Oxygen, ppm	8500	6700	1500	1400	4600	3900
Hydrogen, Wt %	12.74	12.97	12.14	12.65	9.35	10.48
Carbon, Wt %	86.20	86.20	87.35	87.11	89.76	89.00
Hot-Heptane Insol., ppm	680	<10	216	54	180	80
TBP Dist., °F (ASTM D2887)						
St/5	53/156	52/165	69/184	56/179	295/353	295/340
10/30	173/261	178/269	216/375	206/312	449/587	363/538
50	354	356	478	397	653	587
70/90	429/535	424/509	566/706	470/539	710/790	623/668
95/99	602/785	542/603	771/858	571/634	840/941	689/731
Boiling Range, LV%					**	**
St-400°F	60	57	34	51	8 (17)	13 (25)
400-700°F	38	43	55	49	57 (58)	84 (73)
700°F+	2	0	11	0	35 (25)	2 (2)

* Much of the front end (500°F-) was missing from the Wyodak ITSL
oils. The missing fraction represented 24 LV% of the net liquid
product for Syncrude A; 38 LV% for Syncrude B.

** Numbers in parenthesis were corrected for the missing front end.

Figure 2 shows the distillation curves of the Wyodak oils.
[Wyodak H-Coal B is omitted, because only 4% was removed by
distillation. Therefore, its curve would lie close to that Wyodak
H-Coal A, except for the EP which was much lower--603°F instead of
785°F.] Based on information supplied by Lummus, the ITSL curves were
corrected to include the missing front end. As with the Illinois
oils, the Wyodak H-Coal oil contained large amounts of naphtha; the
Wyodak ITSL oil much more middle distillate. The CTSL oils were
intermediate in boiling range and had a more even distribution than
either the H-Coal or ITSL oils.

In general, the two-stage products contained fewer nitrogen- and
oxygen-containing compounds than the single-stage products.
[Exception: Wyodak ITSL A and Wyodak H-Coal contained about the same
amounts of nitrogen.] The H-Coal oils contained considerably more
hydrogen than the ITSL oils, and slightly more hydrogen than the

comparable CTSL oils. Probably, the higher hydrogen content was a result of the higher severity required for the single-stage process. In contrast, Figure 3 shows that within a given boiling range, the two-stage products had higher hydrogen contents than comparable H-Coal oils. Together, these two sets of observations may seem to present a paradox. However, the results are explained by the boiling distributions--the H-Coal oils contained more of the comparatively hydrogen-rich low-boiling components than the two-stage oils.

HYDROTREATING PILOT PLANT TESTS

Discussion. The major goals of the hydrotreating runs were either (1) to make specification jet fuel or diesel fuel and a naphtha suitable for catalytic reforming in a single hydrotreating step; or (2) to make a product suitable for hydrocracking in a second step.

To meet either goal, almost all of the heteroatom contaminants--sulfur, nitrogen, and oxygen--had to be removed by the hydrotreatment. Typically, the control target for product nitrogen content was 0.5 ppm or below. Sulfur is relatively easy to remove compared to nitrogen, and therefore was of little concern in this study. [Although sulfur is much easier to remove than nitrogen, the equilibrium concentrations of sulfur are somewhat higher than nitrogen in products hydrotreated in a single stage.] Oxygen-containing compounds can be as hard or harder remove than nitrogen compounds. However, when the nitrogen was removed to 0.5 ppm, organic oxygen content was also removed to less than 10 ppm (based on limited analytical results). Most of the reported 50-100 ppm oxygen in the products was dissolved water.

In addition to removing the heteroatoms, it is necessary to hydrogenate most of the aromatics compounds in these fractions if finished jet fuel or diesel are to be the main products from a single hydrotreating step. One of the purposes of this work was to show the degree of aromatics saturation needed for specification diesel and jet fuel. The amount of hydrogen consumed will be determined by the hydrogen contents of the feed and products, and the amounts of heteroatoms removed.

If the hydrotreated product is to be hydrocracked, the hydrotreating severity can be somewhat less severe than if jet and diesel fuels are to be finished product. Additional hydrogen will be added in the second-stage hydrocracker.

Catalyst Activity. Table III briefly compares results of hydrotreating results for the syncrudes. The tests were made with a single catalyst, Chevron's commercial ICR-106 catalyst, at three different liquid hourly space velocities (LHSV): 0.5, 1.0, and 1.5 volumes of feed per volume of catalyst per hour, and a variety of hydrogen partial pressures and catalyst temperatures. The syncrudes are listed in approximate order of difficulty (easiest to hardest). All of the oils were not tested at a single set of conditions; therefore, some of the rankings were estimated using results of other tests described in our DOE reports (1). All of the first five syncrudes listed were comparatively easy to hydrotreat, and some rankings were close to one another.

Table III

HYDROTREATING TESTS WITH ICR 106 CATALYST
Syncrudes listed in increasing order of hydrotreating difficulty

LHSV	0.5	1.0	1.5	1.5	1.5	1.5
H_2 Pressure, psia.	2300	2300	2300	1800	1400	1000
Wyodak CTSL B (EP=634°F)						
Temperature, °F	680	705	715	715	715	715
H2 Consumption, SCF/B	775	725	725	690	450	180
Product Nitrogen, ppm	0.5	<0.3	<0.3	<0.3	<0.3	<0.3
Product Aromatics, LV%	3	3	4	6	14	25
Wyodak H−Coal A (EP=603°F)*						
Illinois H-Coal B (EP=589°F)						
Temperature, °F		750	750			
H2 Consumption, SCF/B		2000	1950			
Product Nitrogen, ppm		<0.3	<0.3			
Product Aromatics, LV%		2	5			
Wyodak ITSL B (EP=731°F)						
Temperature, °F	683					
H2 Consumption, SCF/B	1650					
Product Nitrogen, ppm	<0.3					
Product Aromatics, LV%	14					
Wyodak H-Coal A (EP=785°F)						
Temperature, °F		750	750			
H2 Consumption, SCF/B		1225	950			
Product Nitrogen, ppm		<0.3	<0.3			
Product Aromatics, LV%		3	13			
Illinois ITSL B (EP=763°F)						
Temperature, °F	710	730	745	745		
H2 Consumption, SCF/B	1600	1400	950	600		
Product Nitrogen, ppm	<0.2	<0.2	0.4	6		
Product Aromatics, LV%	10	26	38	58		
Illinois H-Coal A (EP=765°F)						
Temperature, °F	750	750	750	750		
H2 Consumption, SCF/B	2150	1600	1275	825		
Product Nitrogen, ppm	<0.3	0.3	10	50		
Product Aromatics, LV%	2	20	35	45		
Wyodak CTSL A (EP=858°F)						
Temperature, °F	750					
H2 Consumption, SCF/B	825					
Product Nitrogen, ppm	0.3					
Product Aromatics, LV%	24					
Illinois ITSL A (EP=859°F)*						
Wyodak ITSL A (EP=941°F)						
Temperature, °F	750					
H2 Consumption, SCF/B	1825					
Product Nitrogen, ppm	4					
Product Aromatics, LV%	42					

* Rank estimated from tests at other conditions (Reference 1).

Some generalizations can be made, based on the ease of hydrotreating and feed properties:

(1) For a given boiling range, syncrudes from two-stage liquefaction are easier to upgrade than those made in one-stage--that is, lower hydrotreating severity is needed for a given product quality in upgrading. This result appears to be the effect of the lower heteroatom contents of two-stage syncrudes.

(2) For syncrudes from a given liquefaction process, relatively small increases in EP can make the syncrudes much harder to upgrade. For example, a good correlation (roughly linear) was found between required catalyst temperature and syncrude EP for a group of ITSL oils, regardless of coal source. For example, Wyodak ITSL B (EP = 634°F) could be hydrotreated at a temperature about 100°F lower than Wyodak ITSL A (EP = 941°F) for the same degree of heteroatom removal. [See Figure 4, Reference 6.]

Not surprisingly, the easiest oils to process were the three syncrudes with EPs below 650°F--Wyodak CTSL light oil (B), and the two redistilled H-Coal (B) oils. The CTSL appears to be the easiest of the three. Although it had a slightly higher EP than the others, it had the advantage of a lower heteroatom content.

Of the four oils with EPs between 700°F and 800°F, Wyodak ITSL oil B had the lowest EP and was easiest. Next is Wyodak H-Coal B. Although it had a slightly higher EP than the oils in this group, it had a much lower average boiling range. Illinois ITSL B ranked next. It was much easier than Illinois H-Coal A, which had about the same EP but a much higher heteroatom content.

Finally, of the three oils with EPs above 800°F, Wyodak CTSL oil A was clearly the easiest. Although its EP was about the same as Illinois ITSL A, it had a lower average boiling range and lower heteroatom content. Of all the oils, Wyodak ITSL A was the most difficult to process. It contained the most 700°F+ material of any of the syncrudes, and had the highest EP (941°F).

Catalyst Stability. The length of specific tests varied from several days to several months. With one exception and within the limits of the tests, ICR-106 catalyst appeared to be stable for heteroatom removal during all of the tests shown in Table III. The exception: With Illinois H-Coal A, the catalyst lost about 20°F of activity during 1100-hr at 1.5 LHSV and 1800 psia hydrogen partial pressure. In contrast, Illinois ITSL B (with about the same EP as Illinois H-Coal A) was stable during a 900-hr test at the same conditions. The difference was probably due to the lower heteroatom and hot-heptane insolubles contents of the ITSL oil. [The higher EP oils were not tested at this pressure, but would be expected to cause appreciable catalyst deactivation also.]

YIELDS

For syncrudes with EPs below 800°F, there was relatively little cracking during hydrotreating, and the feed boiling range determined product boiling range (except for some EP reduction due to hydrogenation). As an example, Table IV contrasts yields of products from Illinois H-Coal A and Illinois ITSL B, two oils that have about the same EP but widely different boiling ranges.

Table IV
HYDROTREATING TO 0.2 PPM NITROGEN (0.5 LHSV, 2300 psia H2)

Syncrude	H-Coal	ITSL
Catalyst Temperature, °F	750	710
Yields, Based on Fresh Feed		
C1-C4, Wt %	0.3	0.2
C5-250°F, LV %	20.4	7.0
250-350°F, LV%	26.3	6.8
350-550°F, LV%	57.7	53.6
550°F+, LV%	6.4	40.6
Total C5+, LV%	111	108
Chemical H2 Consumption, SCF/B	2150	1600
Product Aromatics, LV%	2	12

For higher EP syncrudes, higher hydrotreating severities were required and more cracking occurred. Still, C1-C4 yields were low (2 LV% or below), indicating efficient use of the hydrogen.

PRODUCT PROPERTIES

General Comments. After hydrotreating, products of similar boiling ranges from the different liquefaction processes and different coals were quite similar. After removal of heteroatom-containing compounds, the products mainly consisted of cyclic hydrocarbons. The severity of hydrotreating determined the amount of hydrogenation of aromatics to naphthenes. There were, however, some differences. Products from subbituminous coals contained more paraffins than those from bituminous coals.

Naphtha. Hydrotreated and hydrocracked naphthas from coal liquids are excellent feeds for catalytic reformers because of the high content of cyclic compounds. Paraffin contents of all the hydrotreated naphthas were low, although the Wyodak naphthas contained somewhat more paraffins than those from Illinois coal as shown by Table V.

Table V
PARAFFIN CONTENTS OF TYPICAL 150-350°F HYDROTREATED NAPHTHAS

Feed Source	Paraffins, LV%
Wyodak H-Coal	23
Wyodak ITSL	23
Wyodak CTSL	18
Illinois H-Coal	11
Illinois ITSL	7

At the higher hydrotreating severities, the cyclics in the naphthas were almost all hydrogenated. The naphthenes, however, could be dehydrogenated to high-octane aromatics by catalytic reforming at relatively mild conditions compared to those required for typical petroleum naphthas. Or, when reformed at higher severities, these naphthas would make extremely high octane products for gasoline blending or for chemicals production (benzene, toluene, and xylene). In the reforming process, much of the hydrogen consumed during hydrotreating would be recovered. [We have not performed catalytic reforming studies on naphthas from the two-stage processes, but

results would be expected to be similar to those previously reported for naphthas from single stage processes (7).]

Jet. To make jet fuel meeting the ASTM smoke point specification of 20 mm (minimum), most of the aromatics in the coal liquids had to be hydrogenated.

Figure 4 is a plot of smoke point versus aromatic content of kerosene jet fuels from the various syncrudes. The results fall into two rough groups, those from Wyodak coal and those from Illinois coal. At a given aromatics content, those from Wyodak coal had smoke points 2-3 mm higher than those from Illinois coal, a consequence of the higher Wyodak paraffin content. [The Wyodak jet contained about 10 LV% paraffins; the Illinois jet, 1-3 LV%.] The Illinois jet fuels met the jet smoke specification of 20 mm at 10% aromatics or lower; the Wyodak jet fuels met the specification at about 16 LV% aromatics. [Some of the scatter in results for products from a given coal was due to different boiling distributions. Those jet fuels containing more low boiling material had somewhat higher smoke points.]

Jet fuels from coal offer some unique advantages over those from petroleum. Because they contain high concentrations of naphthenes, they are very dense and have high heating values by volume. Therefore, they could have specialized uses, such as for military fuels. For example, Figure 5 shows the densities of narrow boiling fractions of hydrotreated ITSL oil. Jet fuel of a desired density could be made by adjusting the boiling range. The ASTM specification for jet fuel gravity is 37°API (minimum). However, this specification is probably unnecessary for aircraft with modern flow controllers, and lower gravity (higher density) fuels could be acceptable. Also, these jet fuels have unusually low freezing points, because of low normal paraffin contents.

Diesel. Diesel products from both single-stage and two-stage processes met typical ASTM specifications. A relatively high degree of hydrogenation was needed to meet the cetane-number specification of 40 (minimum).

Figure 6 shows the relationship for cetane number versus aromatics content for products from single-stage and two-stage processes. With the two-stage oils, the specification was met with an aromatics content of about 20 LV%; with single-stage oils, an aromatic content of less than 10 LV% was needed. These differences, however, were not necessarily the result of single-stage versus two-stage processing. Rather, they appear to be due to changes in boiling ranges of the diesels. For example, Table VI compares pairs of samples of different boiling ranges. The aromatics and paraffin contents within a given pair were about the same. Within each pair, the higher boiling sample had the higher cetane number. Also, in other comparisons (1), the more paraffinic diesels had higher cetane numbers, when other properties were about equal.

As with the jet fuels described above, these coal-derived diesel fuels had excellent cold weather properties, and high volumetric energy contents.

Table VI
EFFECT OF BOILING RANGE ON CETANE NUMBER

Source	Initial, °F (TBP)	Midpoint, °F (TBP)	Cetane No.	Aromatics, LV,%	Paraffins, LV%
Wyodak CTSL	250	414	44.2	3.9	9.5
	350	454	48.7	4.6	7.7
Illinois ITSL	250	520	43.1	9.8	<1
	350	538	45.3	11.7	<1
Illinois H-Coal	250	393	35.9	15.6	3.6
	350	438	37.7	18.5	3.7

HYDROCRACKING RUNS

If the feed EP is below 775°F and if diesel fuel is a desired product, further cracking conversion of hydrotreated coal syncrude will probably not be necessary. The EP will be lowered somewhat due to hydrogenation, and little or no hydrotreated product will boil above the diesel range. However, if the feed EP is higher than 775°F or the desired products are either all-gasoline or a combination of gasoline and jet fuel, further conversion may be necessary. In a other papers (8, 9), we discussed in detail the hydrocracking of hydrotreated H-Coal and ITSL oils. Hydrocracking is a flexible process that can be varied to make only naphtha or a combination of gasoline and middle distillate. The products from hydrocracking coal oils are similar to those obtained from hydrotreating; the quantities of each can be varied, depending upon demand.

The liquid yields from hydrocracking were greater from ITSL syncrudes than those from H-Coal or CTSL syncrudes. This is because of the larger fraction of high boiling material in the ITSL syncrude, the lower hydrogen content, and--as a result--the greater volume expansion during hydrocracking. For example, the yield of C5+ naphtha was 115 LV% (based on fresh feed to the first-stage hydrotreater) when when Illinois ITSL B was hydrocracked at 350°F recycle cut point, compared to 108 LV% from Illinois H-Coal A. Thus, 7 LV% more liquid was made from a given volume of ITSL syncrude than from H-Coal syncrude.

TWO-STEP HYDROTREATING OF HIGH EP SYNCRUDES

Specification jet and diesel fuels were made from all of the syncrudes with EPs below 775°F in a single-step by hydrotreating at relatively severe conditions. However, with the three high EP feeds listed at the bottom of Table III, the jet and diesel were either marginal or too aromatic to meet specifications directly--even at 0.5 LHSV and 2300 psia hydrogen pressure .

A series of experiments with Wyodak ITSL A (the most difficult syncrude), suggested an alternative upgrading route.

First, it was shown that the aromatic content increased rather than decreased when the catalyst temperature was increased from 750°F to 775°F. Then, it was shown that the aromatic content remained about the same when the LHSV was reduced by a factor of two (to 0.25 LHSV) and the temperature held constant. Together, these results indicated

that the equilibrium was unfavorable for hydrogenation of some of the high-boiling polycyclic-aromatic compounds at the run conditions.

Therefore, we tried an two-step approach: (1) Hydrotreat at relatively high temperature (e.g., 750°F) to remove most of the heteroatoms. (2) Further hydrogenate at lower temperatures (e.g.,600-650°F) for further aromatics saturation.

In the next test, product from the initial experiment (750°F, 0.5 LHSV, 2300 psia H2), which contained 42 % aromatics, was hydrotreated a second time using the same catalyst. The LHSV and pressure were kept the same, but the temperature decreased to 650°F--100°F lower than previously. Due to the more favorable equilibrium at 650°F, product aromatics were reduced to 12%. The jet and diesel fractions, respectively, exceeded smoke point and cetane number specifications. Also, enough EP reduction was achieved so that less than 5% of the product boiled above the diesel range.

When the temperature was further decreased to 600°F, the aromatic content of the product did not decrease further, but increased to 20%. [The rate of hydrogenation was lower, although the equilibrium was even more favorable than at 650°F.] The diesel fraction still met the cetane number specification, however.

The results show that two-step hydrotreating [with the second hydrotreatment at a relatively low temperature] is an alternative to the hydrotreating/hydrocracking route for upgrading high EP syncrudes, provided diesel fuel is a desired product.

CONCLUSIONS

Coal liquids produced in the ITSL and CTSL processes with EPs from about 600°F to over 900°F were hydrotreated to make diesel and jet fuels, and naphthas suitable for catalytic reforming to gasoline. Specific conclusions are as follows:

(1) Oils from two-stage processes were easier to upgrade than comparable boiling-range products from single-stage processes, due to lower nitrogen and oxygen contents. However, as with products from single-stage processes, relatively small increases in EPs made the oils much harder to upgrade.

(2) Except for modest differences in paraffin contents, properties of finished products of given boiling ranges from both Wyodak and Illinois coals, and both one- and two-stage processes studied were fairly similar, and mainly consisted of cyclic hydrocarbons. Products from Wyodak coal were somewhat more paraffinic than those from Illinois coal.

(3) Product boiling ranges were different, depending upon the liquefaction process and the cut point used in that process. The single-stage processes made more naphtha than the two-stage processes at a given cut point; the two-stage processes made more middle distillate. The ITSL process made more middle distillate than the CTSL process. Diesel products from two-stage processes had higher cetane numbers at a given aromatic content than those from single-stage processes. At least in part, this was due to product boiling range differences.

(4) In all cases studied, the jet fuel and diesel products had high densities and, therefore, high volumetric-energy contents.

(5) Wyodak CTSL light oil had a higher hydrogen content and lower heteroatom content than the other oils. These factors, plus its low EP, made it easier to upgrade than the other syncrudes studied.

(6) For high EP syncrudes, an attractive upgrading route is a two-step process--hydrotreating to remove most of the heteroatoms, followed by low-temperature hydrogenation to saturate aromatics.

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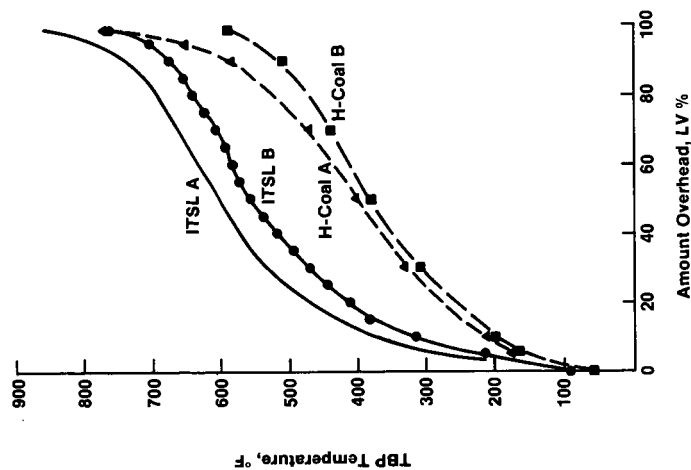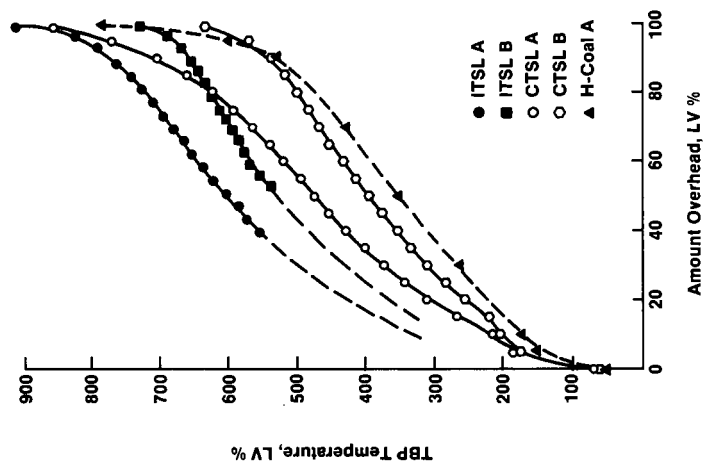# FIGURE 2

TBP DISTILLATIONS OF SYNCRUDES FROM WYODAK COAL

- ● ITSL A
- ■ ITSL B
- ○ CTSL A
- ○ CTSL B
- ▲ H-Coal A

FIGURE 1

TBP DISTILLATIONS OF SYNCRUDES FROM ILLINOIS NO. 6 COAL

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FIGURE 4

EFFECT OF AROMATICS ON SMOKE POINT OF JET FUELS FROM HYDROTREATED COAL-DERIVED FEED

Boiling Range = 250-550°F or 250-600°F

△ Illnois H-Coal
○ Illnois ITSL
■ Wyodak H-Coal
▲ Wyodak CTSL
● Wyodak ITSL

Open Points = Wyodak
Closed Points = Illnois

FIGURE 3

HYDROGEN CONTENT OF SYNCRUDE FRACTIONS VERSUS BOILING RANGE

Hydrogen Content of Whole Oil

Illinois ITSL = 10.68%
Illnois H-Coal = 11.29%
Wyodak CTSL = 12.65%
Wyodak H-Coal = 12.74%

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FIGURE 5

API GRAVITIES OF NARROW BOILING
FRACTION OF HYDROTREATED ILLINOIS ITSL OIL

Total Aromatics, 11 LV %
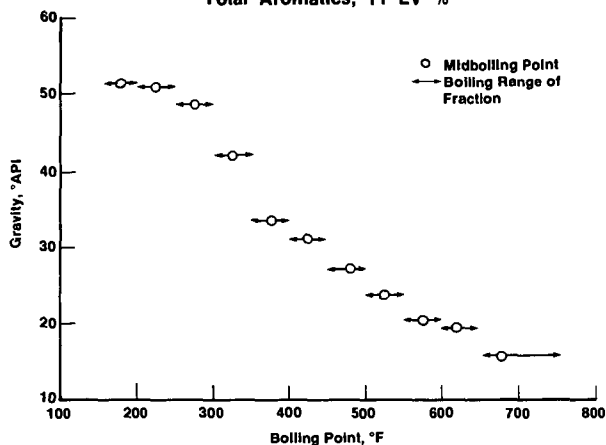
FIGURE 6

EFFECT OF AROMATICS ON THE
CETANE NUMBER OF DIESEL
FUELS FROM HYDROTREATED COAL-DERIVED OILS
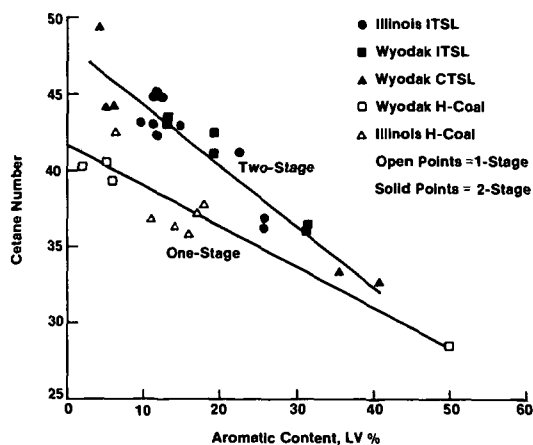
INTEGRATED TWO-STAGE LIQUEFACTION: THE LEGACY AND THE UNFINISHED WORK

ENEO C. MORONI

U.S. Department of Energy, FE-34 GTN, Washington, D.C. 20545

INTRODUCTION

The Integrated Two-Stage Liquefaction (ITSL) concept has received considerable
attention by many laboratories and has emerged as one of the most promising
technology in direct coal liquefaction.

DOE/Lummus/Cities Service, EPRI/Kerr McGee, the Wilsonville teams, Chevron and
Exxon (1) have been in one way or another involved in processes conforming to
the ITSL concept, each one with a somewhat different approach or processing
scheme. Recently, HRI (2) has developed another staged liquefaction concept
which recently has received DOE support for extended continuous bench-scale
testing.

Major achievements were obtained during the development of the ITSL process at
Lummus, from May 1980 to June 1985, which have changed substantially our
approach to coal liquefaction techniques and inspired new thoughts in
unraveling the mechanism of direct coal liquefaction at low severity opera-
tions. These novel mechanistic considerations need to be supported with
further studies using suitable model compounds, some of which have been
recently proposed (3).

Several papers have reported the early development of the ITSL process and
related projects (4-8). This paper has the objective to divulge the most
recent achievements of an evolved ITSL process, pointing out the unfinished
work, and to expand the concept of the low-severity staged approach which
resulted from the evolved ITSL process and emerged as the most desirable
pathway for the direct production of marketable liquid fuels from coals.
The ultimate objective is to interest the researchers dedicated to
fundamentals of coal liquefaction toward the technological needs and the
understanding of reaction mechanism, kinetics and thermodynamic limitations
residing with the novel, low-severity staged coal liquefaction approach.

THE ITSL LEGACY

Major accomplishments obtained at low-severity operations in a 3/4 ton/day
ITSL process development unit at Lummus and from related bench-scale studies
in various laboratories, include:

    Low severity produced extracts are low in heteroatoms and more
    easily hydrogenatable, consistently yielding excellent equilibrium
    donor solvent (9).

    No high viscosity gel region is apparent over the 280-350°C
    temperature range for a slurry of bituminous coal and ITSL
    solvent, as was the case for slurries prepared with the same
    coal and other types of solvent (10).

Low severity processing forms mostly reactive low molecular-weight fragments. Conversely, single stage thermal and thermal/catalytic processing produce high-molecular weight products thought to be actually condensation products of such smaller fragments and consequently, less reactive (11).

Proton NMR analysis, modified to provide data on ITSL distillate and non-distillate fractions, has been shown to be useful in the development of a kinetic model for coal extract hydroprocessing, thus enabling us to distinguish catalytic hydrogenation and cracking reactions, and to predict the solvent donor capability as well as the yield structure of the upgraded products (12).

A mixture of condensed aromatics, hydroaromatics, paraffins and their respective heteroatom derivatives is produced during coal liquefaction. This mixture tends to be unstable because of the incompatibility between polar heteroatom compounds and hydrocarbons, as well as between condensed aromatics and paraffins. Condensed hydroaromatics, having closer affinity for both aromatics and paraffins, tend to keep them in solution, thus contributing to the stability of the coal extract. Low severity coal extraction yields a larger quantity of hydroaromatics and small amounts of high heteroatom, condensed aromatics and paraffins (12).

Best catalysts tested are those modified to suppress the hydrocracking activity and enhance hydrogenation functionality (9).

Coal derived transportation fuels, produced by refining of distillate from low severity operations, possess inherent high quality which is due mostly to their hydroaromatic (naphthenic) nature. Coal derived naphthas contain large quantities of highly alkylated cyclohexanes which, by reforming, convert to the corresponding benzenes and in the process, recover a large portion of the hydrogen to make the overall coal liquefaction approach economically more attractive. Alkylated benzenes are the major contributors to the high octane gasoline thus formed. Coal derived middle distillate is constituted mostly of di-and tri-hydroaromatics and corresponding aromatics.

Further refining has been successfully employed to convert some of the aromatics to meet marketable jet and diesel specifications of smoke point and cetane number, respectively (13).

From the operation of the process development unit (PDU) at Lummus (9) the following important results were obtained:

Subbituminous coal was demonstrated to be an attractive feed for direct liquefaction: The distillate yield was slightly lower (2.9 bbl/ton of moisture-ash-free coal compared to 3.2 for bituminous coals) but its lower cost, higher reactivity in the second stage and its ease in being converted to a lighter product

are over-riding features in its favor. In addition, ITSL with
Wyodak coal demonstrated good operability in both reaction stages
and was easily deashed.

When the deasher is placed after the LC-Fining reactor, the
distillate yield was increased seven percent. More importantly,
the LC-Fining catalyst was unaffected by ash feed and reactor
volume is unchanged.

Most of the LC-Fining reactor volume could be replaced by a fixed
bed hydrocracking unit. This resulted in an equally good yield
of -650°F product with no loss in hydrogen efficiency. The
-650°F product contained less than 100 ppm sulfur and less than
500 ppm nitrogen, making this a clean, light and environmentally
acceptable product. Furthermore, this flow configuration reduces
the second stage reactor volume by at least 18 percent and may
also greatly simplify and reduce the cost of the deashing section.

The SCT reaction was operated at 500 and 1000 psig, with no
adverse effect on yields or hydrogen usage. This leaves the LC-
Fining as the only high pressure section of the process.

Analysis of the results indicated that a commercial SCT reactor
can be designed to retain all the important features of the PDU.
There is every reason to believe that SCT can be scaled to
commercial size.

Deasher bottoms were coked to produce additional liquid products.
The liquid yield was about 20 percent of the organic matter in
the ash-rich feed.   '

Low temperatures of about 700°F, do not provide sufficient
hydrogenation to replenish solvent quality, while at 800°F the
solvent contains insufficient transferable hydrogen. Therefore,
the optimum temperature for both conversion and regeneration of
recycle solvent is about 724-750°F (9).

In antisolvent deashing experiments, THF-insoluble/quinoline-
soluble preasphaltenes precipitate consistently with the mineral
matters, whereas the THF-soluble preasphaltenes do not. This
indicates that THF-insoluble preasphaltenes may be the major cause
of mineral matters agglomeration, increasing their diameter and
causing the particles to settle faster (14).

THE UNFINISHED WORK

The most significant achievements of the ITSL program came into focus during
the last part of the ITSL project and of the related projects before they
ceased operation. In this particular period, those who closely monitored
the overall program, gathered the large set of data made available, and
structured them for suitable process engineering and economic evaluation,

became aware of an evolutionary trend in coal liquefaction processing. The major factors contributing to this novel trend were: 1) the better understanding of the very sensitive interdependency between the stages of coal extraction, of the coal extract upgrading and hydrogen donor recycle solvent requirements, which emerged only from the data produced in a continuous, integrated recycle mode of operations, and 2) the more favorable results of low-severity operations, practically solving, in an easy and elegant manner, most if not all the problems encountered by using high-severity operations which were practiced in earlier processes, i.e. German, H-Coal, SRC-II, etc.

But perhaps more important to the fundamental research community is the fact that the large set of ITSL data under scrutiny for process development, lacks the fundamental data to support the profound changes in the mechanism and kinetics occurring at low-severity coal liquefaction.

Some of the concepts and technology needs are outlined below.

Preservation of highly reactive, small fragments in the coal extract is of utmost importance in producing an excellent donor solvent and high quality distillate fuel products. For this purpose, the fragments should be withdrawn from the extraction reactor as soon as they are formed. The unconverted coal can be further converted by recycling it with the preasphaltenes as part of the recycle solvent.

Better preservation of the reactive small fragments can be achieved by increasing the donatable hydrogen level and decreasing the heteroatom content of the recycle solvent. It is important for the superior hydrogen donor solvent to penetrate the less reactive macerals. Consequently, it is advisable to allow for a thermal soaking treatment, i.e., at 250-350°C temperature range for 10-30 minutes, prior to the short contact time (SCT) reaction of rapid heating (two minutes) to the 450°C exit temperature. It is evident that all the above activities are interdependent and the improvements maximized in an integrated recyle process.

It is extremely difficult to capture in research bench scale units the essence of the results produced in the integrated recycle process, because most of the key benefits, i.e., coal conversion and enhanced donor solvent quality, are obtained only after several cycles of the integrated staged operations. Bench scale researchers could avoid the long and tedious recycle operations by applying the aforementioned kinetic model for coal extract hydroprocessing (12) and using proton-NMR data of the coal extract to predict solvent donor capability and yield structure of the upgraded products.

Proton-NMR analysis is rapid, requires small samples, is highly reliable and has excellent reproducibility.

Removal of the heteroatoms in the early stage of coal extraction is desirable and ought to be sequential, removing first the more abundant oxygen and thus making easier the subsequent nitrogen removal.

Complementary fundamental studies on C-O and C-N bond scission should be emphasized over the current C-C bond cracking effort.

Most of the sulfur is converted to hydrogen sulfide during the two above sequences, and the H_2S must be kept in the system as catalyst itself and as "activator" of transition metal catalysts.

It is essential that the ITSL technology be pursued to the completion of the evolutionary trend which became almost dormant with the termination of most of the ITSL projects. It is up to the fundamental research community to fill-up the gap of supportive fundamental research through studies of thermodynamics, kinetics and reaction mechanisms involved in low-severity operations which are part of the ITSL process. Of particular interest would be the matching of reaction kinetics of dehydrogenation of the hydrogen donor solvent with the hydrogen acceptancy of coal extracts.

Those of us involved in these efforts are optimistic about the future of low-severity direct coal liquefaction and the quite similar coal/oil co-processing as the practical approaches in helping to alleviate an increasingly energy-deficient world.

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Comparative Economics of Two-Stage Liquefaction Processes

David Gray, Glen Tomlinson, Abdel El Sawy and Abu Talib

The MITRE Corporation, 1820 Dolley Madison Blvd. McLean, Va. 22102

Background

It has been recognized in research and development carried out by Lummus-Crest (1), that two stage liquefaction provides an attractive route to coal liquefaction by optimizing the discrete stages in conversion of solid coal to distillate. While improvements in process efficiency, product yield and quality have been demonstrated, the current limited kowledge of coal structure and liquefaction chemistry still necessitates empirical testing of process alternatives.

A number of promising process alternatives have been developed and are under current investigation at a bench or process development unit (PDU) scale by a number of contractors under DOE sponsorship. The contractors include Lummus-Crest, Southern Services (Wilsonville) (2), Hydrocarbon Research Inc., (3) and Amoco (4). The process variations under current investigation are as follows:

- Production of a major part of the distillate product in Stage 1 versus Stage 2.
- Catalytic first and second stage versus thermal first stage and catalytic second stage.
- Critical Solvent Deashing versus Anti-Solvent Deashing.
- Direct coupling of Stages 1 and 2 without intermediate deashing.

DOE requested that MITRE undertake a comprehensive technical and economic analysis of all the two-stage coal liquefaction configurations currently under development in order to quantify the improvements made in the production of high quality distillates from coal. Table 1 lists the processes that were analyzed in this task. The methodology used to perform this analysis was as follows:

- Review test data. Select most representative run for each process using both Illinois #6 and Wyoming coals.
- Scale test data to develop material balances for conceptual commercial plants processing 30,000 tons per day of moisture free coal to the liquefaction units.
- Identify unit operations for commercial plants.
- Compute coal and energy requirements for plant balance.
- Estimate capital and operating costs for commercial plants.

- Compute annual revenue requirements based on consistent economic assumptions.
- Compute product costs required to satisfy revenue required.

Results and Discussion

Table 2 shows the characteristics of the commercial-scale plants for both Illinois No. 6 and Wyoming coals. Plants with high yields and/or high hydrogen consumption require large quantities of additional coal for steam and hydrogen production.

The construction costs of the conceptual commercial plants were estimated using an 1981 UOP/SDC (5) commercial design of the Lummus Integrated Two-Stage Liquefaction (ITSL) plant as a basis for costs of unit operations, where possible. Costs of unit operations not addressed in this report were obtained from other sources. Operating and maintenance costs were estimated using a standard procedure developed by UOP/SDC. The annual revenue requirements for these plants were then calculated based on the capital recovery and operating costs developed from use of consistent economic assumptions.

Since each process configuration produces a syncrude having a different quality, it was decided to account for this product quality difference. In order to do this, MITRE has calculated the hydrogen requirements and volume gain which occur when the C_4-850°F raw output of each plant is hydrotreated to produce a heteroatom-free, 35°API, 13-percent hydrogen product. The cost of this hydrotreatment is calculated based on the assumption that the cost of hydrogen production and addition is $1.00/pound.

Product costs were then computed to satisfy the annual revenue requirements based on the following assumptions. It was assumed that heavy products (i.e., 850°F+ products) were valued at one-half of the value of a barrel of C_4-850°F liquid product. For the hydrocarbon gases (C_1-C_3), it was assumed that 12×10^6 Btus were equivalent in value to one barrel of C_4-850°F product.

Figure 1 shows comparisons of the annual revenue requirement, equivalent product yield, and required selling price of products from the conceptual commercial plants when operated with Illinois No. 6 coal. All values are shown as percentages of the Lummus Integrated Two-Stage Liquefaction (ITSL) base case. For comparative purposes two conceptual plants based on single-stage processes (H-Coal (6) and EDS (7)) are included.

The bars depicting annual revenue requirements are divided into four sections, to illustrate the relative contribution of capital recovery, coal, operating and hydrotreating costs. The capital recovery costs for the two-stage plants vary by about 2 percent, indicating a similarly small variation in the capital costs of the plants. Capital costs of the single-stage plants are 5.4- and 9.5-percent lower than the Integrated Two-Stage Liquefaction (ITSL) base case for H-Coal and EDS, respectively.

The variation in hydrotreating costs reflects variation in both the quality of the raw product and the quantity of the C_4-850°F fraction. Hydrotreating costs of EDS are lower than the other systems, because of the relatively low yield and high API quality of the raw EDS product. The total annual revenue requirements vary from a low of 89.7 percent of base for EDS, to a high of 107.5 percent of base for CTSL.

The equivalent barrels of yield show a much wider variation than the annual revenue requirements. EDS yield is lowest at 84.6 percent of base, while CTSL is highest at 115.7 percent.

The lower portion of Figure 1 compares the required selling price of hydrotreated products from the conceptual plants. The prices vary from 105.9 percent of base for EDS to a low of 92.9 percent of base for CTSL, a spread of 13 percent. The most advanced systems, e.g., modified Lummus, Wilsonville RITSL, and CTSL, offer the lowest product prices. All these systems catalytically treat an ash-containing extract. It is doubtful that the one-percent difference between CTSL and RITSL is significant. However, the slight superiority of these systems relative to the modified Lummus is believed to be significant and is traceable to the higher rejection of soluble material which is inherent in the deashing system employed at Lummus. Lummus has suggested that the additional liquids in the deashed overflow could be recovered by coking.

Figure 2 shows economic comparisons for plants operated with Wyoming coal. Capital recovery cost variations between the plants are very similar to those observed in the Illinois No. 6 plants. The total revenue requirements vary from 93.8 to 100 percent of base for the two-stage plants, but are much lower at 89 and 83.3 percent of base for the single-stage H-Coal and EDS plants, respectively.

Plant yields show a much greater variation than was observed in the plants processing Illinois No. 6 coal. Yields vary from a low of 91.6 percent of base for EDS to a high of 141.5 percent of base for CTSL.

The required selling prices also show a wide variation. The Lummus ITSL shows the highest selling price at 100 percent of base, while CTSL offers the lowest price at 68.9 percent of base. The single-stage H-Coal and Wilsonville DITSL processes offer similar prices of 80.3 and 80.7 percent of base, respectively.

The results with both Illinois No. 6 and Wyoming coals indicate that the additional cost and complexity of two-stage processing is justified by the increases in yield and product quality which can be obtained.

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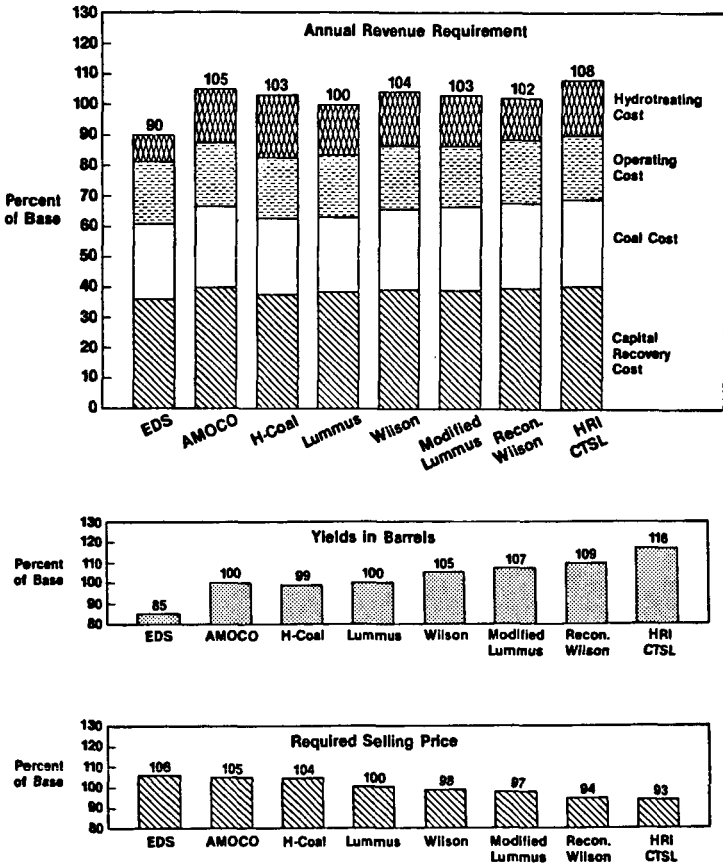FIGURE 1: COMPARISONS OF ILLINOIS NO. 6 COAL PLANTS
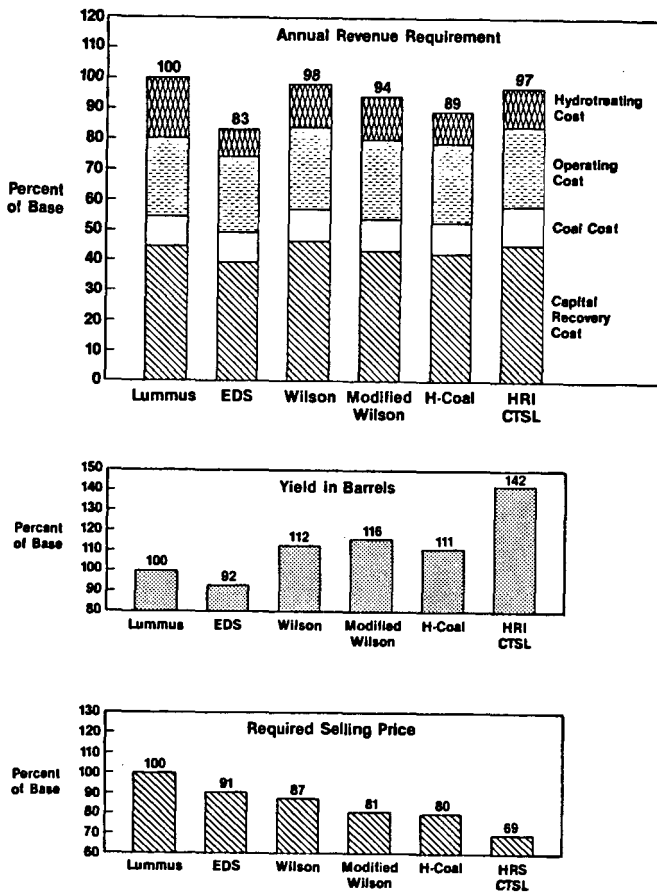
FIGURE 2:   ECONOMIC COMPARISONS OF WYOMING COAL PLANTS

TABLE 1:   TWO-STAGE PROCESSES

Process	Scale	Stage I	Deashing	Stage II
Lummus-Crest Integrated Two-Stage Liquefaction (ITSL)	600 Lb/Day	Thermal	Anti-Solvent	Catalytic
Wilsonville Two-Stage Liquefaction	3 T/Day	Thermal*	Critical Solvent Deashing	Catalytic
Hydrocarbon Research, Inc. Catalytic Two-Stage Liquefaction (CTSL)	50-100 Lb/Day	Catalytic	No Deashing Between Stages	Catalytic
AMOCO Thermal/Catalytic Two-Stage Liquefaction	50-100 Lb/Day	Thermal	No Deashing Between Stages	Catalytic

*Sometimes Slurry Catalyst Used

TABLE 2:   CONCEPTUAL COMMERCIAL PLANT SUMMARIES

ILLINOIS NO. 6 COAL FEED

Process:	Lummus ITSL	Wilsonville ITSL	Wilsonville RITSL	Modified Lummus ITSL	AMOCO	CTSL
Input						
Steam Coal, TPD (MF)	2,000	2,000	2,000	3,000	3,000	3,000
Gasifier Coal, TPD (MF)	0	3,000	4,000	2,000	2,000	4,000
Total Plant Coal, TPD (MF)	32,000	34,000	37,000	35,000	35,000	37,000
Output						
SNG, MMSCFD	0	0	12	11	50	25
Raw C_4 + Liquid, BPSD	90,000	105,000	105,000	95,000	94,000	108,000
Total Liquid Yield after Hydrotreatment, BPSD	101,000	114,000	113,000	106,000	100,000	117,000

WYOMING COAL FEED

Process:	Lummus ITSL	Wilsonville ITSL	Wilsonville DITSL	CTSL
Input				
Steam Coal, TPD (MF)	3,000	2,000	2,000	4,000
Gasifier Coal, TPD (MF)	0	3,000	4,000	9,000
Total Plant Coal, TPD (MF)	33,000	36,000	36,000	43,000
Output				
SNG, MMSCFD	33	28	6	3
Raw C_4 + Liquid, BPSD	70,000	90,000	97,000	114,000
Total Liquid Yield after Hydrotreatment, BPSD	80,000	94,000	98,000	119,000

Temperature-Staged Catalytic Coal Liquefaction

Frank Derbyshire, Alan Davis, Mike Epstein, and Peter Stansberry

College of Earth and Mineral Sciences
The Pennsylvania State University
University Park, PA   16802, USA

Abstract

    Coal liquefaction has been investigated under conditions where reaction is conducted in successive stages of increasing temperature and in the presence of a dispersed sulfided Mo catalyst. This sequence leads not only to high conversions but also greatly increases the selectivity of the products to oils at the expense of asphaltenes, with only marginal increase in gas make. The product distribution is strongly influenced by the solvent composition and the reaction conditions in the two stages. Examination of the liquefaction residues from the liquefaction of a bituminous and a subbituminous coal has provided supporting evidence to show that the temperature-staged reaction sequence favors hydrogenative processes. Moreover, the choice of reaction conditions for optimum performance is rank-dependent; for example, low-rank coals appear to require a lower first stage temperature than bituminous coals in order to minimize the potential for regressive reactions.

Introduction

    In some earlier reported research (1,2) a bituminous and a subbituminous coal were pretreated by dry catalytic hydrogenation, using a molybdenum catalyst at $350^\circ C$ for 1 h, following which they were mixed with naphthalene (2:1 solvent to coal ratio) and reacted at $425^\circ C$ for 10 min. The results showed that the low-temperature pretreatment improved both the net coal conversion, based upon solubility in tetrahydrofuran, and the product distribution. Notably, the oil to asphaltene ratio was substantially increased with only marginal additional gas make.

    Based upon these findings, further research has been directed to investigating the chemistry and the potential of temperature-staged coal liquefaction. The results of this research are presented in this paper. Similar studies are being conducted on a larger scale by Hydrocarbon Research Inc. (3).

Experimental

    Coal Preparation

    Samples of bituminous and subbituminous coal were provided by the Penn State Coal Sample Bank for use in this research. The coals were obtained undried and in lump form about 12 mm size and were crushed in a glove box under oxygen-free nitrogen to 0.8 mm top size. The crushed coals were subdivided by riffling into a number of 10 g representative samples and sealed in vials under nitrogen. Properties of the coals are shown in Table 1.

    The coals were impregnated with Mo catalyst by slurrying with an aqueous solution of ammonium tetrathiomolybdate in the concentration necessary to attain a loading of 1% wt Mo on a dmmf basis. The quantity of coal impregnated was sufficient for a complete series of experiments. After slurrying, the excess water was removed by vacuum freeze-drying.

    Liquefaction

    The impregnated coal was mixed in a ratio of 1:2 with liquefaction solvent. In most of the experiments, naphthalene was selected as the solvent because, at least

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at the onset of reaction, no H-donor would be present, which would allow the effects of added catalyst and low-temperature coal pretreatment to be more clearly discerned. Approximately 0.1 g of CS_2 was added to the reaction mixture to ensure that the molybdenum was maintained in the fully sulphided state.

Reactions were carried out in tubing bomb reactors of about 30 cm^3 capacity which were heated by immersion in a fluidized sandbath. More detailed descriptions of the experimental procedures have been given elsewhere (4). Reactions were conducted either at 425°C for 10 min or under these same conditions after first pretreating at 350°C for 60 min. The initial hydrogen pressure (cold) for both pretreatment and the higher temperature reaction was 7 MPa.

When the low-temperature pretreatment was carried out, the bombs were quenched to room temperature at the end of the reaction period and the yields of light gases were determined by volumetric measurement and gas chromatographic analysis. The main purpose of the cooling and venting procedure was to ensure that there was a high partial pressure of hydrogen in the reactor at the beginning of the higher temperature stage. The rationale for choosing a short reaction time for the high-temperature stage (10 min at 425°C) was the same as that used for solvent selection; namely to accentuate the effects which would be caused by the low-temperature reaction.

Following high-temperature reaction, the gas yield and composition were determined and the solid and liquid products were worked-up to obtain the yields of insoluble residue (tetrahydrofuran, THF) asphaltenes (hexane-insoluble, THF-soluble) and oils (hexane-soluble). In these calculations, it was assumed that the naphthalene reported to the hexane-solubles. Despite extensive precautions, some of the lighter liquefaction products were lost during product work-up and especially during the removal of solvents. Oil yields are therefore calculated from the mass balance assuming that most of the mass balance deficit is attributable to the loss of light ends.

A further factor, which is not accounted in the product distribution, is the yield of water produced by reaction. It is not anticipated that this will constitute more than a few percent of the liquid yields, even with the subbituminous coal, although firm estimates have not yet been made. Because of the method of calculation of the oil yield, any water which is produced is considered as oil. Consequently, the actual oil yield will be somewhat lower than reported.

A few experiments were conducted to explore the effects of extended reaction time at 425°C and the influence of a more reactive solvent than naphthalene. In the latter instance, the solvent was a process-derived recycle solvent fraction (454+°C) obtained from the Lummus Integrated Two-Stage Liquefaction (ITSL) process, when operating on Wyodak subbituminous coal.

In determining the product distribution, quantities of oil and asphaltene, equivalent to those present in the original solvent, were subtracted from the product yields in order to obtain the net yields attributable to coal.

Residue Microscopy

The dried liquefaction residues (THF insolubles) were embedded in epoxy resin and polished with a series of alumina slurries. Examination was undertaken with a polarizing reflected-light microsope under oil immersion at a magnification of 625; a rotatable compensation plate was used as an aid in distinguishing between isotropic and anisotropic materials. Some observations were made in blue-light irradiation, in order to observe the proportions of liptinite macerals present.

Results and Discussion

Reactions in Naphthalene

The conversions and product distributions obtained by the liquefaction of the subbituminous and bituminous coals under various combinations of pretreatment and liquefaction reactions are summarised in Tables 2 and 3. Similar trends are apparent for both of the coals. Reaction in the presence of the catalyst produced higher net conversions than the 'thermal' experiments, as would be expected. However, the combination of low-temperature catalytic pretreatment followed by the higher temperature catalytic reaction had the greatest influence in improving the product selectivity concomitant with attaining the highest conversion. In particular, the highest oil yields were obtained without any attendant increase in the production of light hydrocarbon gases.

An examination of the liquefaction products by gas chromatography showed that there was no significant conversion of naphthalene to tetralin (less than 1%) in any of these experiments. While this finding does not exclude the possibility that the catalyst may promote liquefaction through the successive generation and dehydrogenation of donor solvent, it does suggest that other reaction pathways are operative and may be more important.

The addition of catalyst, without pretreatment, significantly increased the conversion of both coals over that obtained in the thermal experiments. At the same time, these conditions produced the lowest oil yields and the lowest ratios of oils to asphaltenes. The pretreatment evidently allows the catalyst to perform certain functions which ultimately lead to higher oil yields and these functions appear to be not as readily performed during a short catalytic reaction at the higher temperature of 425°C.

Microscopic Examination of Liquefaction Residues

There were notable differences in the appearance of the residues from the bituminous and subbituminous coals. The bituminous coals hydrogenated in the absence of catalyst showed clear evidence of the development of plasticity, i.e., rounded particle outlines and the formation of spheres of vitroplast. Vitroplast is a low-reflecting, isotropic, pitch-like material, usually derived from vitrinite, that occurs as spheres and agglomerates (5). The vitroplast observed in this study is the type which Shibaoka (6) has referred to as a primary vitroplast, being derived directly by softening of vitrinite.

In contrast, the residues derived from the catalytically hydrogenated bituminous coals had apparently undergone more extensive reaction. There was no evidence of simple melting, and the vitrinite-derived material was considerably reduced in volumetric proportion relative to that of other macerals. The reflectance of this vitrinite-derived material was lower than either that of the vitrinite in the feed coal or that of the vitroplast in the residues of uncatalyzed runs. These observations are consistent with the action of the catalyst being instrumental in the hydrogenation and breakdown of the vitrinite structure. An unexpected feature of the residues was the large proportion of remaining, although not necessarily unchanged, liptinite (sporinite and cutinite) present in samples from the catalysed experiments with bituminous coal.

None of the residues from the subbituminous coal contained vitroplast or showed other evidence of plasticity during treatment. Rather, the residues of the vitrinite (huminite) consisted of tattered skeletons of the structures present in the original coal. However, the vitrinite reflectance was significantly higher in the residues than in the parent coal; that of the residue from the catalysed and pretreated coal was judged to be somewhat lower than that of other residues. This

run also resulted in more particle disintegration than was observed in the other residues.

The microscopic studies of the liquefaction residues reflect the trends shown by the yield data in confirming that the staged catalytic liquefaction produced the conditions most conducive to coal hydrogenation and liquefaction.

From the residue analysis for the subbituminous coal, it appears that the temperature selected for the low-temperature stage was too high as shown by the increase in reflectance of the vitrinite-derived materials in the residues relative to the vitrinite (huminite) in the untreated coal. In contrast, the residues from catalysed bituminous coal hydrogenation display the predominance of hydrogenation reactions as evidenced by the lower vitrinite reflectance compared to the parent coal. Without catalyst, the very obvious development of plasticity indicates the dominating effect of thermal treatment.

Effect of Other Reaction Conditions

The data presented above have illustrated the potential advantages to be derived by liquefying coals in stages of increasing temperature and in the presence of a catalyst. Verification of these phenomena has been demonstrated more comprehensively and on a larger scale by Hydrocarbon Research Inc. (3).

In the laboratory scale studies, no systematic attempt has yet been made to investigate how independent variables such as the reaction conditions in the first and second stages, the solvent composition and the catalyst type and concentration affect the performance attainable in such a reaction sequence. Some preliminary data are presented in Figure 1 which show the comparative affects on the product distribution for the subbituminous coal (PSOC-1401) due to (i) increasing the high temperature residence time from 10 to 45 min while employing naphthalene as solvent and (ii) using the more reactive process solvent and the 45 min high-temperature residence time.

With naphthalene, increasing the reaction time at high-temperature is evidently advantageous in promoting further interconversion of oils to asphaltenes (the oil to asphaltene ratio increased from 0.8 to 2:1) with some simultaneous increase in gas make; the CO_x yield increased from 7.9 to 9.8% and the yield of C_1-C_4 hydrocarbons increased from 0.8 to 3.0%. As in the other experiments using naphthalene as solvent, there was no significant conversion of naphthalene to tetralin.

A much more dramatic change in product selectivity was achieved by using the process solvent when the oil to asphaltene ratio increased to approximately 14:1. To offset this gain there was a more significant increase in gas make; the CO_x and C_1-C_4 yields being 12.2 and 4.7%, respectively. Quite evidently, the composition of the solvent is an important parameter even in the presence of an active catalyst.

Acknowledgements

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TABLE 1

Coal Properties

Penn State Sample Bank No.	PSOC-1266	PSOC-1401
Seam	L. Kittanning	Lower Wyodak
County	Mahoning	Campbell Co.
State	Ohio	Wyoming
Province	Eastern	Northern Great Plains
ASTM rank class	hvAb	sub. B. (apparent)
Moisture content, % wt (a.r.)	3.4	16.3
Mineral Matter, % wt dry coal	6.1+	6.6*
Elemental Composition % dmmf		
C	83.2	74.3
H	5.0	5.2
O**	8.6	19.3
N	2.1	1.1
S	0.5	0.2
Maceral Analysis, % vol		
Vitrinite	91	85
Exinite	3	2
Inertinite	6	13
Sulfur Forms (% dry coal)		
Organic	0.46	0.19
Pyritic	0.79	0.01
Sulfate	0.02	0.00
Total	1.27	0.20

+By low-temperature ashing; *Reported as ASTM "Ash"; **By difference

TABLE 2

Product Yields from the Liquefaction of Subbituminous Coal (PSOC 1401)

Conditions		Product Yields (% dmmf)								
Pretreatment	Liquefaction	Conversion	Asphaltenes	Oils[1]	CO^2	CO_2^2	$C_1-C_4^2$	CO^3	CO_2^3	$C_1-C_4^3$
a) None	Thermal	42.5	4.7	28.8	--	--	--	0.6	7.9	0.5
b) Thermal	Thermal	41.9	9.9	22.1	0.2	7.3	0.1	0.4	9.3	0.2
c) None	Catalytic	66.7	41.8	17.6	--	--	--	0.5	6.3	0.5
d) Catalytic	Catalytic	90.7	46.7	35.3	0.3	6.5	0.3	1.1	6.8	0.8

TABLE 3

Product Yields from the Liquefaction of Bituminous Coal (PSOC 1266)

Conditions		Product Yields (% dmmf)								
Pretreatment	Liquefaction	Conversion	Asphaltenes	Oils[1]	CO^2	CO_2^2	$C_1-C_4^2$	CO^3	CO_2^3	$C_1-C_4^3$
a) None	Thermal	58.1	42.8	13.7	--	--	--	0.3	0.9	0.4
b) Thermal	Thermal	59.0	47.3	10.2	0.03	0.9	0.05	0.2	1.1	0.24
c) None	Catalytic	72.6	66.7	4.8	--	--	--	0.2	0.6	0.3
d) Catalytic	Catalytic	77.3	36.8	38.8	0.09	0.5	0.06	0.3	0.8	0.6

Conditions: 2/1 solvent (naphthalene) to coal (dmmf); catalyst MoS_2, 1% wt dmmf; pretreatment 350°C, 1 h, 7 MPa H_2 (cold); liquefaction 425°C, 10 min 7 MPa H_2 (cold).

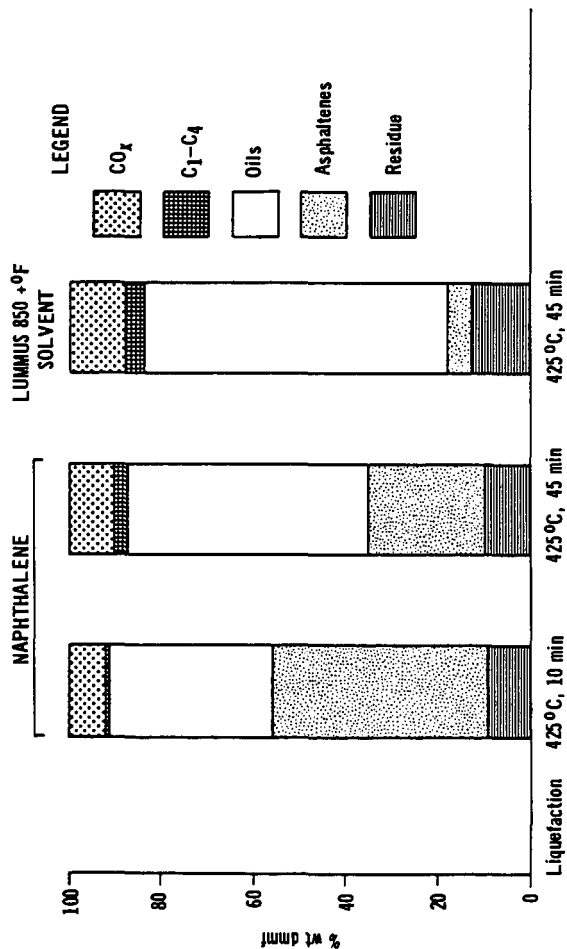[1]By difference; [2]After pretreatment; [3]Net yield (pretreatment + liquefaction)

Figure 1. INFLUENCE OF LIQUEFACTION CONDITIONS AND SOLVENT COMPOSITION ON TEMPERATURE STAGED CATALYTIC LIQUEFACTION; SUBBITUMINOUS COAL, WYODAK (PSOC–1401) Pretreatment 350°C, 1h, 7 MPa H_2, 1% wt MoS_2

TWO-STAGE COAL LIQUEFACTION
WITHOUT GAS-PHASE HYDROGEN

H. P. Stephens

Sandia National Laboratories
Albuquerque, New Mexico 87185

INTRODUCTION

Current two-stage direct coal liquefaction processes require the use
of high-pressure purified hydrogen to hydrogenate either the solvent
or a coal/solvent slurry. This paper describes techniques to
eliminate the direct use of hydrogen gas in the solvent production
and primary coal liquefaction stages. The approach employs the
water-gas shift (WGS) reaction to generate liquefaction hydrogen-
donor solvents at low temperatures and pressures in a catalytic
solvent production stage, followed by reaction of the solvent with
coal, in the absence of hydrogen, in a thermal primary liquefaction
stage.

Previous researchers (1,2) have used mixtures of carbon monoxide and
steam to convert coal in single-stage processes operated at high
temperatures (380^o to 475^o C) and pressures (to 5000 psi). Although
pilot tests with high-reactivity, low-rank coals achieved moderate
conversions to benzene-soluble products, yields of distillate oils
were low (3).

In an initial portion of this study it was proposed (4) that a
significant improvement in coal liquefaction using CO/H_2O mixtures
may be realized by separating, or staging, the WGS-solvent
production and coal liquefaction reactions, allowing each to be
performed at an optimum temperature. Results of thermodynamic
calculations and preliminary experiments proved that use of low
temperatures (<300^o C) favors solvent hydrogenation via the WGS
reaction, thus allowing the use of low pressure (500 psi). In
contrast, high temperature kinetically favors the reactions involved
in coal liquefaction--coal molecule bond rupture and transfer of
hydrogen from donor solvent compounds to coal moieties. This paper
describes the results of flow reactor experiments to produce a
liquefaction solvent at space velocities comparable to actual
processes, and use of this solvent to liquefy coal. Both of these
steps have been accomplished without the use of hydrogen feed gas,
and high conversions of a bituminous coal have been achieved.

EXPERIMENTAL

Two series of experiments, described briefly here and in more detail
in the following sections, were performed. The first consisted of
production of a coal liquefaction solvent, rich in hydroaromatics,
via the WGS reaction in a catalytic flow reactor at low temperature
and pressure. In the second set of experiments coal was thermally
liquefied in batch microreactors without gas-phase hydrogen using
the solvent produced in the flow reactor.

Materials

Feeds to the WGS-solvent production reactor consisted of carbon monoxide, deionized water and a nearly saturated mesitylene solution of polynuclear aromatic hydrocarbons (weight basis PAH's: 11.6% phenanthrene, 12.0% pyrene and 16.7% fluoranthene). Mesitylene was chosen as the solvent for the PAH's because of its relatively low vapor pressure (75 psi at 240° C), its ability to dissolve large amounts of PAH's at room temperature, and its stability under high temperature coal liquefaction conditions. Extrudates (0.8 mm diameter by 4 mm length) of Shell 324M, a 2.8 wt. % Ni, 12.4 wt. % Mo on alumina catalyst, were used in the WGS-solvent production reactor. Prior to use, the catalyst was presulfided, in-situ for six hours, with 10 mole % H_2S in H_2 at 385° C and atmospheric pressure.

Liquefaction reactions were performed with a bituminous coal, Illinois #6 (Burning Star Mine--proximate analysis: 3.7% moisture, 9.4% ash, 34.5% volatile and 52.4% fixed carbon; dry basis ultimate analysis: 72.5% C, 4.7% H, 1.0% N, 0.1% Cl, 2.9% S, 9.8% ash, and 9.0% O by difference; mineral matter content: 13.7%).

Apparatus and Procedure

WGS-solvent production was performed in a concurrent flow trickle-bed reactor consisting of six 1.0 cm ID by 15 cm long catalyst-filled stainless steel tubes connected in series. Each tube was filled with 10.5 g of catalyst. The reactor was contained in a forced-air convection oven thermostatted to $\pm 1.0°$ C. Reactor pressure was controlled with a precision back-pressure regulator and gas and liquid products were sampled subsequent to pressure letdown. After pressurizing to 500 psig with CO, the reactor temperature was ramped to 240° C at 10° C/min and water flow was initiated. Upon detection of conversion of CO/H_2O to CO_2/H_2, PAH solution flow was started. Carbon monoxide, water and the PAH solution were delivered to the reactor at weight hourly space velocities of 0.124, 0.079, and 0.48 g-feed/hr/g-catalyst, respectively. For the WGS reaction, the amount of water delivered was one percent in excess of that required by stoichiometry to ensure that conversion was limited only by thermodynamic equilibrium. It was estimated from the reactor void volume and fluid flow rates that the residence time of the gas was two minutes and that of the liquid phase was approximately sixty minutes.

Prior to use for the liquefaction reactions, the solvent produced by the flow reactor was concentrated by nearly a factor of two by evaporation of mesitylene under vacuum. This higher concentration, which allowed the use of lower solvent to coal ratios for the liquefaction reactions, could be achieved because of the increased solubility of the hydroaromatics formed in the flow reactor.

Coal liquefaction reactions were performed in batch microautoclaves with slurry capacities of 8 cm^3 and gas volumes 35 cm^3(5). Four reactors could be operated simultaneously. After the reactors were charged with coal and solvent, they were pressurized to 450 psig with nitrogen. They were then heated to 445° C for 36 min (time at temperature) in a fluidized sand bath while being agitated with a wrist-action shaker at 200 cycles/min. Following the heating

period, the reaction vessels were quenched in water, the final temperatures and pressures were recorded, a gas sample was taken, and the product slurry was quantitatively removed for analysis. All experimental variables for both the flow and batch reactors were monitored and recorded with a computer-controlled data acquisition system.

Four coal liquefaction reactions were performed. To test the impact of amount of donatable solvent hydrogen on coal conversion, three reactions were performed with WGS-produced solvent to coal ratios of 2:1, 3:1, and 4:1. A control experiment, without donatable hydrogen, was performed with a portion of the flow reactor PAH feed solution, which contained no hydroaromatics. The control experiment had a "solvent" to coal ratio of 3:1.

Product Analyses

On-line analyses for the partial pressures of CO and CO_2 in the gas stream from the flow reactor were performed with a Hewlett-Packard 5710A gas chromatograph. Prior to analysis, residual water vapor was eliminated from the gas sample with a cold trap. The partial pressure of hydrogen was obtained by the difference between the sum of the CO and CO_2 pressures and the sample pressure. Gas samples from the liquefaction reactions were analyzed for N_2, H_2, CO, CO_2, and C_1-C_4 hydrocarbons with a Carle series 500 gas chromatograph with a hydrogen transfer system.

The amounts of PAH's and hydroaromatics in the flow reactor feed and liquid product samples were determined with a Hewlett-Packard 5890 capillary column-equipped gas liquid chromatograph. Coupled gas chromatography/mass spectrometry techniques were used to identify the order of elution of the PAH's and hydrogenated PAH's.

Conversion of coal to products was quantified by tetrahydrofuran (THF) and n-heptane (C_7) solubility. Dry, mineral matter free (dmmf) basis conversions were calculated from the difference between the weight of organic coal and the insoluble organic matter resulting from THF or C_7 extraction of the product. In addition, the C_7 soluble materials, which contained the post-reaction solvent components, were examined by capillary column chromatography to determine the extent of dehydrogenation of solvent hydroaromatics.

RESULTS AND DISCUSSION

WGS Solvent Hydrogenation

The performance of the WGS-solvent production reactor can be evaluated in terms of conversion of CO/H_2O to CO_2/H_2, and the extent of hydrogenation of the PAH's.

From the gaseous product analyses, the conversion of CO/H_2O to CO_2/H_2 was observed to be 97%. This is significantly greater than the value of 92% calculated from the initial partial pressures of CO and steam and the pressure equilibrium constant (6) for 240° C. The observed larger conversion results from removal of hydrogen due to hydrogenation of the PAH's, which causes an additional shift to

products. Thus, coupling the WGS and solvent hydrogenation reactions promotes efficiency for the WGS reaction.

The extent of hydrogenation of the PAH's can be seen in Figure 1, which shows a comparison of the chromatogram of the feed solution to that of the product. Analysis of the product solution showed that 31% of the phenanthrene, 49% of the pyrene and 92% of the fluoranthene were converted to hydroaromatics. From the amount and distribution of the hydroaromatics and the extent of the WGS reaction, it was calculated that 30% of the hydrogen generated was used to produce hydroaromatics. The liquid product was found to contain 0.52 wt. % donatable hydroaromatic hydrogen. The solvent for the coal liquefaction reactions, concentrated by removal of mesitylene from the flow reactor product, contained 0.87 wt. % donatable hydrogen, a high value by current process standards.

It is notable that almost complete conversion of fluoranthene to hydrofluoranthenes (primarily tetrahydrofluoranthene, which accounted for half of the donatable hydrogen) was achieved, while only half of the pyrene and a third of the phenanthrene were hydrogenated. For pyrene (Py), the limitation for conversion to dihydropyrene (H_2Py) is a thermodynamic one. The equilibrium ratio of $[H_2Py]/[Py]$ may be calculated from the reactor outlet hydrogen partial pressure (155 psia) and the pressure equilibrium constant (7) at 240° C, 0.0042/psia. The calculated value of 0.65 is in agreement with the observed value of 0.66, indicating that the concentration of dihydropyrene was limited by thermodynamics, rather than kinetics. The production of hydrophenanthrenes may also be thermodynamically limited, though no thermodynamic data are available for comparison. Although the WGS-solvent production reactor yielded high concentrations of hydroaromatics, previously reported work (7) indicates that even better performance can be achieved with a more active catalyst at lower temperatures, where formation of hydroaromatics is favored.

Coal Liquefaction

The effectiveness of the coal liquefaction reactions performed without gas phase hydrogen can be judged by the conversion of the coal to THF and C_7 soluble products, and to C_1-C_4 hydrocarbons; by the amount of hydrogen transferred from hydroaromatic hydrogen donors to the coal; and by the percentage of hydrogen lost from the solvent to the gas phase.

Table 1 presents a summary of the results of the liquefaction experiments. As can be seen, the conversion of coal was dependent on solvent hydrogen availability. For the control experiment (No. 1), containing no donatable hydrogen, the THF and C_7 conversions were very low: 30% and 17%, respectively. However, all the experiments with WGS-produced solvent, containing hydroaromatics, yielded much higher conversions, which increased with increasing solvent to coal ratio. The 4:1 solvent to coal experiment (No. 4), resulted in the highest THF and C_7 conversions, 98% and 48%, respectively. The C_1-C_4 hydrocarbon gas make for the experiments with the WGS-produced solvent (Nos. 2-4) were low, nominally 3%.

The fate of the donatable hydroaromatic hydrogen in the solvent was determined from the amounts in the solvent before reaction with coal H_b, that remaining in the solvent after reaction with coal H_a, and that transfered to the gas phase H_g. The percentage donated to the coal H_c can be calculated by difference:

$$H_c = 100 \times \frac{H_b - H_a - H_g}{H_b} .$$

From the values for H_g in Table 2 it can be seen that the utilization of hydrogen was efficient, as only 10% of the donatable hydrogen was lost to the gas phase, the balance being donated to the coal or remaining with the solvent. It is also noted from the values of H_a that nearly all of the donatable hydrogen was depleted from the solvent. In fact, experiment No. 2 with a 2:1 solvent to coal ratio was clearly hydrogen starved, resulting in the lowest THF and C_7 conversions for the experiments with WGS-produced solvent. In contrast, experiment No. 4, with a solvent to coal ratio of 4:1 had sufficient donatable hydrogen to achieve high conversions, as evidenced by the 20% donatable hydrogen remaining after completion of the reaction.

PROCESS IMPLICATIONS

The results of the experiments presented in this paper clearly demonstrate that coal can be effectively liquified without the use of high-pressure purified hydrogen feed gas. This suggests that substantial economic improvements in direct coal liquefaction can be achieved. Figure 2 shows a schematic flow diagram for a two-stage liquefaction process proposed on the basis of these results. Notable differences between this and current two-stage processes are: 1) elimination of high-pressure purified hydrogen for solvent production; 2) use of low temperature in the solvent production reactor; 3) elimination of gas-phase hydrogen and high pressures in the thermal liquefaction reactor; and 4) selective recycle of solvent components (primarily PAH's). Use of this process would eliminate the requirements for a separate WGS reactor and gas separation units for hydrogen production, and high pressure equipment for solvent production and liquefaction reactors. Because these units account for approximately half of the estimated $1.5 billion capital investment of a 50,000 barrel/day plant, this process would result in substantial savings in capital costs. Operating costs such as those for compression of gases would also be significantly lower.

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Figure 1.   Comparison of high resolution gas
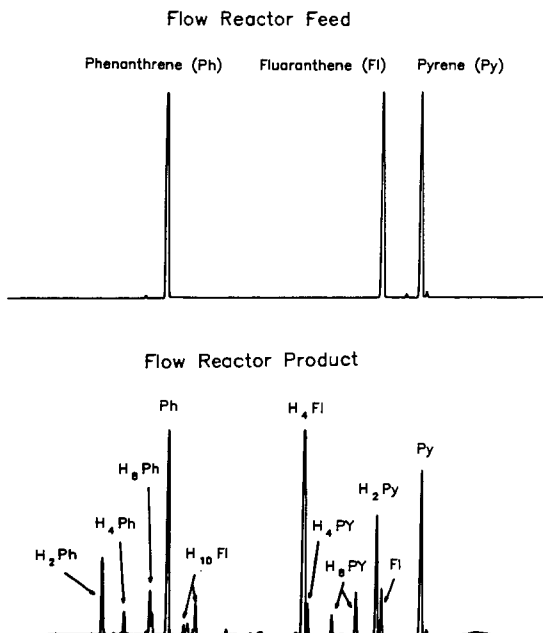liquid chromatograms of the flow reactor feed
and product solutions.

Flow Reactor Feed

Flow Reactor Product

Figure 2.   Schematic flow diagram for a two-stage
liquefaction process via WGS-solvent production.
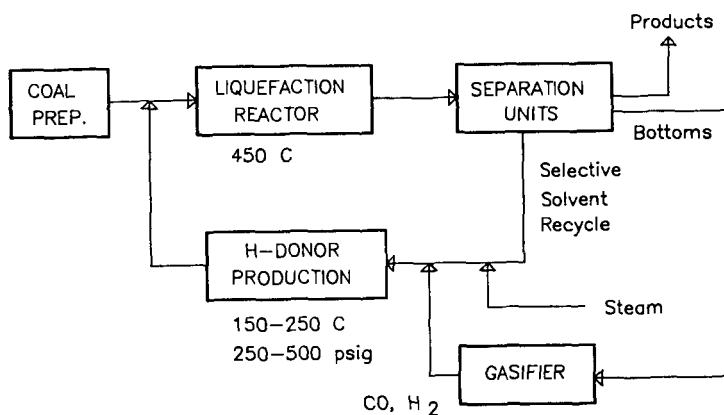
TABLE 1

Results of Coal Liquefaction Experiments [a]

Exp. No.	Solvent: Coal	Conversions (% dmmf basis)			Solvent Hydrogen Balance (% donatable hydrogen)		
		THF	C_7	$C_1 - C_4$	To Coal	To Gas	Remaining
1[b]	3:1	30	17	1.6	--	--	--
2[c]	2:1	91	21	2.9	90	9	1
3[c]	3:1	97	42	3.1	84	11	5
4[c]	4:1	98	48	3.1	69	11	20

a)   Reaction conditions for all experiments: 445 C, 36 min,
     450 psig cold charge nitrogen. No gas-phase hydrogen used.

b)   Performed with flow reactor feed solution. PAH's only;
     no donatable solvent hydrogen.

c)   Performed with WGS-produced solvent.

ENHANCED COAL LIQUEFACTION WITH STEAM PRETREATMENT

P.R. Bienkowski, R. Narayan, R.A. Greenkorn and K.C. Chao[*]

School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907

SUMMARY

A two step process for the liquefaction of coal, in a semi-flow micro reactor, was investigated. The process consisted of pretreating coal with low temperature steam, followed by treatment with supercritical steam. The maximum observed conversion of a Wyodak subbituminous coal, using this two step process, was 40 wt% on a moisture and ash free basis (MAF). The $240\,^\circ$C pretreatment step resulted in a 32% increase over the conversion observed with just a $400\,^\circ$C treatment. The coal liquid obtained has a number average molecular weight of 325 and a mass average molecular weight of 373, with a narrow molecular weight distribution. The hydrogen and oxygen content of the extract is increased, a significant amount of the oxygen is present as dihydroxyl aromatics. A highly condensed residue of lower hydrogen and oxygen content is obtained which can be of value as a solid fuel.

INTRODUCTION

Recent investigations have led to the observation (1) that in its native unweathered state coal is a reactive material, far from being the inert solid that it is commonly regarded. Extensive hydrogen bonds connect the poly nuclear aromatic cluster to form a semi-permanent macro molecular structure. The structure is particularly fragile in sub-bituminous coals, and may be subject to rupture with mild treatment to dissociate the hydrogen bonds. Graff and Brandes (2) found that carbon conversion to liquids in pyrolysis at $940\,^\circ$C was raised from 23% to over 50% if the coal was exposed to steam for times less than 30 minutes at temperatures between about 320 and $360\,^\circ$C. Both pretreatment and pyrolysis were conducted in 50 atm of steam. This result suggests that coal is partially depolymerized by the steam pretreatment, perhaps by the removal of oxygen linkages. If this is indeed the case, improved yields and/or lighter liquids should result if the pretreated coal is liquefied instead of pyrolyzed.

EXPERIMENTAL

Wyodak coal was pretreated and treated with steam in a semi-flow micro reactor at controlled conditions to exclude oxygen. The apparatus is depicted in Figure 1. The main components are a Milton Roy metering pump (29 to $290cm^3/hr$) which provides a continuous and constant flow of distilled deoxygenated water to the reator, a Tecam fluidized sand bath (model SBS-4) controlled with a Leeds and Northrup controller (Electromax III), a Helicoid pressure gauge (0 to 3000 PSIG), an autoclave micro metering valve and a micro reactor equipped with a sheathed thermocouple (see Figure 2).

The feed material was an unweathered subbituminous Wyodak coal provided by EPRI in a water slurry kept in a sealed air-tight barrel (#4171). Table 1 shows the elemental analysis of samples taken from this barrel. Samples A and B were taken from the top and middle of the barrel and were suction dried for use. These were the main feed material. About a 50 gm sampled of this material was removed from the barrel and vacuum dried; a sample of this material is repoted as sample C. A few reactions were carried out with this material.

The suction dried coal was prepared in a Buchner filter, by applying suction to it for about one hour. The top portion of the material was removed from the filter and thoroughly mixed to insure a homogeneous sample for reaction. The moisture content of this material ($\approx$ 30 wt %) was determined by weighing a sample before and after further drying in a vacuum oven at $45\,^{\circ}C$ for 6 hours. Duplicate samples were used for moisture determinations.

Suction dried Wyodak coal is paste-like, and is messy to bandle. A free-flowing coal powder was obtained for reaction experiments by drying the coal in vacuum under mild heating. The vacuum dried coal was prepared by suction drying in a Buchner funnel over nitrogen; the material was then transferred in a jar filled with nitrogen, to a vacuum oven and dried for 72 hours at $45\,^{\circ}C$. The experimental reaction procedure for vacuum dried coal was similar to suction dried coal except that the separate moisture determination of the dried coal was no longer necessary.

To prepare for reaction the oven dried micro reactor (see Figure 2) was weighed and then filled with about 4 gm of wet suction dried coal or 3 gm of vacuum dried coal and reweighed for an accurate determination of the quantity of material charged to the reactor. The charged reactor was fitted into the apparatus upon connecting tubings and fittings. The system was purged of air by flushing with nitrogen. Enough water was pumped from the buret into the reactor to raise the pressure to 50 psia, about 10 to $12cm^3$ being required. The reactor was lowered into the sand bath, the pressure adjusted to 750 psia with the aid of the micro metering valve, as water was pumped into the system at $0.4cm^3/min$. The steam generated in the heating coil passed through the reactor, was condensed, and collected in an Erlenmeyer flask.

At the termination of an experiment the reactor was removed from the sand bath, and placed in a vacuum oven over night at $45\,^{\circ}C$ to remove any water. The reactor was then weighed, the contents were removed and placed in a predried and weighed thimble. The reactor was then reweighed, the

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change in weight being compared to the weight gain of the thimble.

The coal in the thimble was extracted with toluene for 4 to 6 hours in a Soxhlet apparatus. The thimble was dried over night in a vacuum oven and reweighed to detemined the amount of coal extracted. On selected runs the effluent collected in the Erlenmeyer flask was extracted with chloroform and sent to analysis.

The only time the coal sample was exposed to oxygen of the air was during suction drying at ambient temperature. Oxygeń was carefully excluded from the reaction system. Feed water to the reactor was deoxygenated by blowing it with nitrogen. >From the time of steam pretreatment the reactor remained tightly closed and completely isolated from air until the reactor was cooled down after steam treatment. The only coal that was heated before reaction was that which was vacuum dried at 45 ° C. The suction dried coal was never heated.

EXPERIMENTAL RESULTS

Table 2 shows the conversion of Wyodak coal upon pretreatment and treatment with steam at 750 psia. Treatment and pretreatment (if used) steps each lasted 30 minutes. Conversion expresses the fraction of coal that was extracted by the steam from the reactor plus the fraction that was extracted by toluene from the Soxhlet apparatus. The toluene extraction was small, ranging from 0% to less than 3% of the total reported conversion. Toluene extraction was incorporated in our experimental procedure in order to put our experimental results on the same basis with those of other investigators (3,4,5,6) who wash their coal residue with toluene.

With suction dried coal, when not pretreated, treatment with steam at 200 ° C gives a practically zero (2.2%) conversion. Raising the treatment temperature to 400 ° C raises the conversion to 30.5%. Pretreatment with steam at 200 ° C further raises the conversion to 38.5%. Raising the pretreatment temperature to 240 ° C raises the conversion to 40.3%. This is the highest conversion observed in this work, for, upon raising the pretreatment temperature to 320 ° C conersion is lowered to 33.8%. Raising the treatment temperature to 430 ° C further lowers the conversion to 34.2%.

The conversion of vacuum dried coal is reported in the second part of Table 2, and is generally lower than the corresponding results for suction dried coal. Even the mild heating at 45 ° C during vacuum drying made the coal more refractory. Comparison of the results obtained with the two different coal samples convinced us to stop using vacuum dried coal. All other experiments reported here used suction dried coal.

The conversions reported in Table 2 were obtained with 750 psia steam for both the pretreatment and treatment. The effect of steam pressure at the treatment stage was investigated, the results are reported in Table 3. Holding the pretreatment pressure constant at 750 psi, an increase in treatment pressure from 750 t0 2500 psia, produced a slight reduction in the observed conversion. Higher pressure apparently increases the rate of retrograde reactions. This effect more than compensates for any increase

in solvent power of the steam at a higher pressure, leading to reduced extraction.

Twenty five experiments were performed in all. The conversions in Tables 3 and 3 represent average values for experiments at the same conditions.

CHEMISTRY

Extract and residue samples from two experiments, Runs 5 and 27, were analyzed by infrared spectroscopy, NMR and 'FIMS. Run 5 consisted of a 320 ° C pretreatment followed by a 430 ° C treatment, while Run 27 was at 200 ° C and 400 ° C.

Table 4 shows the elemental analyses of the extract and the residue of Run 27. The analysis of the feed coal is also shown for comparison. The extract has a higher H/C ratio (1.28) as compared to the feed coal (0.95), whereas the residue has a lower ratio (0.68). The O/C ratio follows a similar pattern, being higher in the extract (0.32) than in the feed (0.28), and lower in the residue (0.13).

The steam pretreatment/extraction process produces a hydrogen-rich extract which contains oxygenated compounds and heteroatomic species of the original coal, leaving behind a more condensed aromatic residue.

The same trend is indicated for nitrogen and sulfur, being enriched in the extract and reduced in the residue. But here because of the small amounts, especially of nitrogen, accuracy is low.

The infrared spectrum of the steam extract of Run 27 is shown in Figure 3. The IR spectrum is dominated by broad, strong -OH stretching vibrations in the 3400-3100 cm^{-1} region. The presence of sharp aliphatic -OH bands just below 3000 cm^{-1} suggests that the extract contains aliphatic material, and reinforces the observed enrichment of H and O in the extract.

Further confirmation is provided by the [1]H NMR spectrum of the steam extract from Run 5 shown in Figure 4. The ratio of H_{ar}/H_{sat} is 1:30. 43% of the H_{sat} hydrogens are associated with methylene, methine, or methyl groups which are not directly bonded to aromatic nuclei. Another 20% of the H_{sat} appearing as a group of signals in the 2-3 ppm region are associated with hydroaromatic structures or associated with methyl, methylene and methine groups directly attached to an aromatic nucleus. The dominant sharp signal at 1.2 ppm is characteristic of long chain polymethylene groups. Thus, one of the major constituents of the hydrogen rich extract is aliphatics present primarily as long chain polymethylenes, either as free species or attached to aromatic/hydroaromatic ring systems.

The ^{13}C NMR spectrum (Figure 5) is dominated by a number of well resolved lines riding on a spectral envelope in the 15-80 ppm region which is the normal chemical shift region for aliphatic compounds, supporting the presence of significant quantities of aliphatic materials in the steam extract. The most intense signal is at 30.2 which is generally assigned to the internal methylene carbons $(C_1-C_2-C_3-C_n-)$ of straight chain alkanes corroborating the presence of long chain polymethylene groups (minimum average carbon chain length; $n_c \approx 8-10$) which may or may not be attached to an

aromatic ring.

The group of signals in the 15-20 ppm region is probably due to the methylene carbons attached to aromatic rings. The presence of a broad spectral envelope in addition to the sharp alkane lines demonstrate the extract's complexity. The spectral complexity is due to the presence of small amounts of polymethylene type compounds. The complex band of carbon signals in the 120-130 ppm region is due to the aromatic and polycyclic aromatic species. Interestingly, a small, but distinctive signal occurs at 179 ppm which is where the carbonyl carbon of a -COOH group appears suggesting the presense of some carboxylic acids in the extract.

Field ionization mass spectometry (FIMS) is a mass spectometry technique which uses a soft ionization mode and allows most molecules to be observed as unfragmented molecular ions. The method can provide a true molecular weight profile for any given complex mixture. Figure 6 represents the field ionization mass spectrum of the extract. The extract has a very narrow molecular weight distribution with number average (M_n) and weight average (M_w) molecular weight of 315 and 373, respectively. Since 75% of the material was volatilized in the FIMS probe the observed molecular weights are a true representation of the extract and the extract is composed of low molecular weight compounds. The most prominent peaks in the spectrum appear at m/z 110, 124, and 138 and can be assigned to dihydroxyl benzene and its methyl and ethyl analogs, respectively. Suprisingly no prominent peaks due to monohydroxyl benzene (phenol) or its C-1 or C-2 analogs are found. The oxygenated compounds present in the extract are best represented by the class of dihydroxyl benzenes and other dihydroxyl aromatics. There are a number of other prominent peaks in the higher molecular weight range which, in all probability, arise from the polymethylenes attached to an aromatic ring (identified by NMR) but the FIMS analysis does not allow ready identification of these compounds.

The presence of reactive components like the polymethylene species, the dihydroxyl benzenes, and the low molecular weight profile of the extract suggests that the coal is very reactive and not a highly condensed, very large molecular weight, intractable molecule. Self condensation and crosslinking reactions of the dihydroxyl aromatics, alkylation of the activated aromatic rings by the polymethylene species in the coal , are some of the retrogressive reactions that these coals can undergo, under the severe processing conditions generally employed.

Pretreatment with steam, at lower temperatures, allows the breaking of hydrogen bonds, loosening up the coal matrix, and stabilizing some of the reactive components in the coal. When the temperature increases during the supercritical extraction step, many of these reactive molecules can be steam volatilized or steam extracted, escaping the loosened coal matrix structure before undergoing retrogressive reactions. This explanation is supported since the introduction of a low temperature pretreatment step before the supercritical steam extraction leads to a 32% increase in conversion.

The presence of reactive dihydroxyl benzenes in the extract is also supporting evidence. Dihydroxyl aromatics have never been reported as occuring in coal liquids obtained under normal coal processing

conditions generally employed. They cannot survive the severe processing conditions. Small amounts of dihydroxyl aromatics have been obtained in flash or fast pyrolysis conditions. The very rapid heating allows the dihydroxyl aromatics to escape the coal matrix before they can undergo retrogressive reactions.

CONCLUSIONS

The steam pretreatment-extraction process produces enhanced extractan yields. The extract has a high H/C ratio due to the presence of long chain polymethylene compounds which may or may not be attached to aromatic rins. The extract contains significant amounts of oxygenated compounds, some of which are present as dihydroxyl aromatics. A highly condensed residue (low H/C ratio) is obtained which can be attractive as a solid fuel for combustion.

ACKNOWLEDGEMENTS

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TABLE 1

ANALYSIS OF WYODAK COAL

SAMPLE	A Wet	B Wet	C Vacuum Dried
Carbon	59.51	59.72	58.17
Hydrogen	4.79	4.13	4.35
Oxygen	17.90	22.44	18.94
Nitrogen	0.79	0.76	0.63
Chlorine	-	-	-
Sulfur	2.97	2.55	3.07
Ash	13.59	13.47	16.46
TOTAL	99.55	103.07	101.62
BTU/lb	10,614	-	10,141

Analysis of samples was performed by Huffman Laboratory.

TABLE 2

Conversion of Wyodak Coal upon Pretreatment and Treatment with Steam at 750 psig

Pretreatment Temp °C	Treatment Temp °C	% Conversion MAF
Suction dried coal		
None	200	2.2
None	400	30.5
200	400	38.5
210	400	40.3
320	400	33.8
320	430	34.2
Vacuum dried coal		
None	400	27.3
200	400	38.4
240	400	34.0

TABLE 3

Effect of Pressure of Treatment Steam on Conversion

Pretreatment Treatment	Temperature: 200°C Pressure: 750 psia Temperature: 400°C
Pressure of Treatment Steam, psia	% Conversion MAF
750	38.5
1500	38.6
2500	36.9

TABLE 4

Elemental Analysis of Extract, Residue, and Feed of Run 27

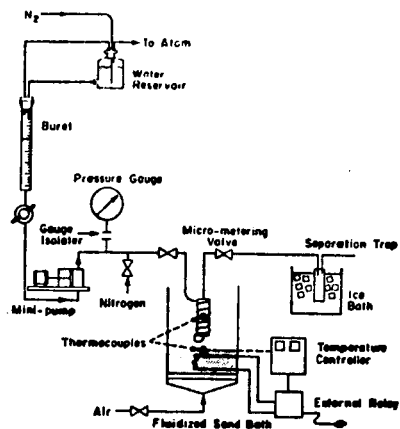| Wt %	Extract	Residue	Feed
C	54.21	64.97	59.72
H	5.77	3.69	4.13
O	23.42	11.20	22.44
N	4.08	1.01	0.76
S	4.30	2.75	2.55
Ash	8.04	17.55	13.47
Atomic Ratio			
H/C	1.28	0.68	0.95
O/C	0.32	0.13	0.28

Figure 1: Experimental Apparatus
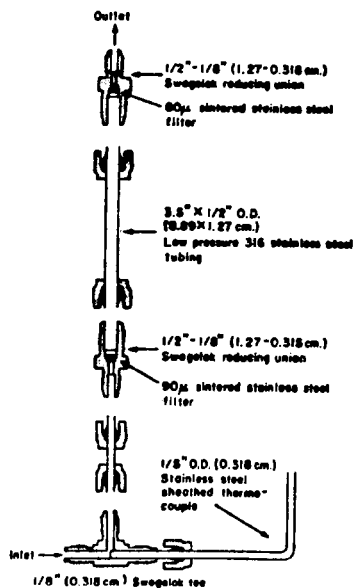
Figure 2: Exploded View of Micro-reactor

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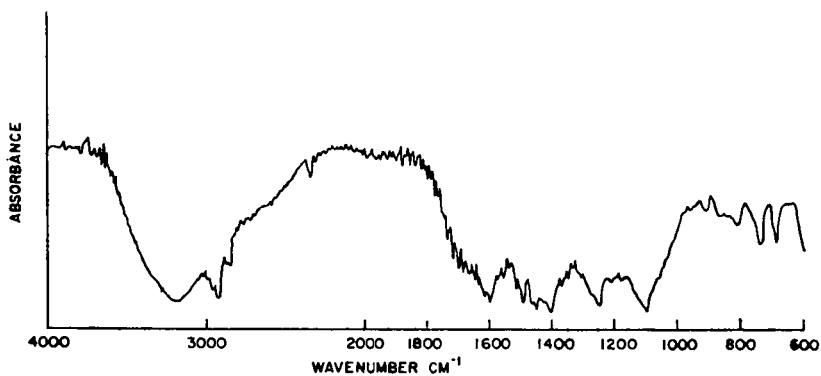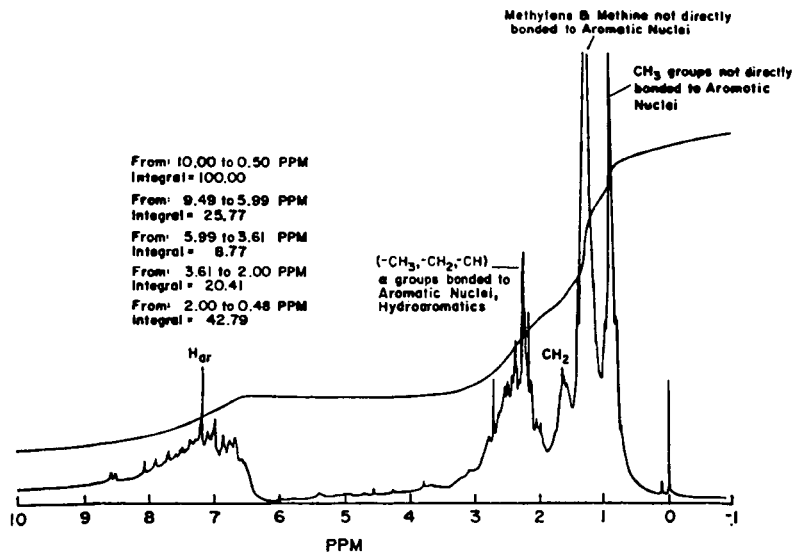
Figure 3: Infrared Spectrum of Steam Extract of Run 27

Methylene & Methine not directly
bonded to Aromatic Nuclei

CH₃ groups not directly
bonded to Aromatic
Nuclei

From: 10.00 to 0.50 PPM
Integral = 100.00

From: 9.49 to 5.99 PPM
Integral = 25.77

From: 5.99 to 3.61 PPM
Integral = 8.77

From: 3.61 to 2.00 PPM
Integral = 20.41

From: 2.00 to 0.48 PPM
Integral = 42.79

(-CH₃,-CH₂,-CH)
α groups bonded to
Aromatic Nuclei,
Hydroaromatics

CH₂

H$_{ar}$

Figure 4: 470 MHz ¹H NMR Spectrum of Steam Extract of Run 5
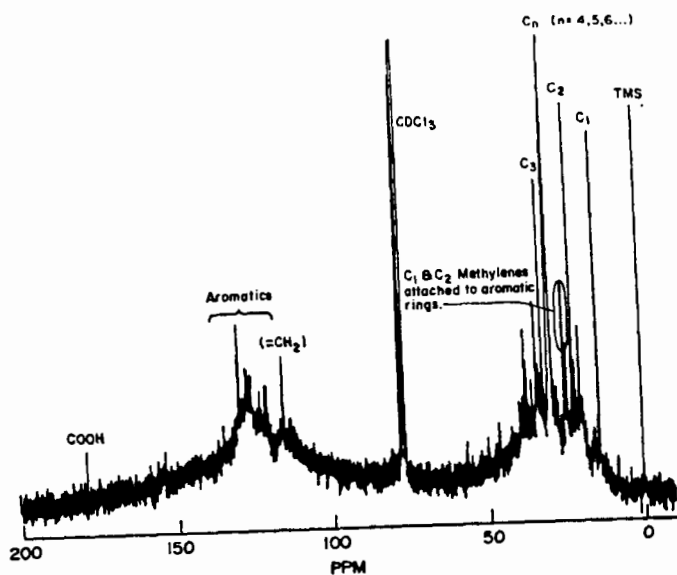
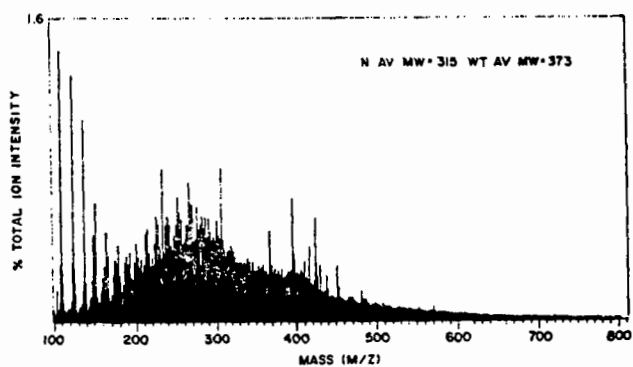Figure 5: ^{13}C NMR Spectrum of Steam Extract of Run 5

Figure 6: FIMS of Steam Extract of Run 5

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THE EFFECT OF REACTION CONDITIONS ON SOLVENT LOSS
DURING COAL LIQUEFACTION

Bruce R. Utz and Sidney Friedman

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, PA 15236

INTRODUCTION

The fate of a coal-liquefaction recycle solvent during Integrated Two-Stage Liquefaction (ITSL) and other direct liquefaction processes is a major concern. If the solvent has an inadequate concentration of hydrogen donors or other solvent components that might enhance liquefaction, then the quality of the solvent will be degraded and conversion to liquid products will be adversely affected. Studies using the solvents phenol (1), tetrahydroquinoline (2-4), quinoline (5), and pyridine (6) have shown that these compounds are partially incorporated by covalent bonds, but a relatively large amount is hydrogen bonded to coal-derived products. In other studies using pure ^{13}C- and ^{14}C-labeled aromatic or hydroaromatic compounds as solvents (3,6-8), the amount of adduction was determined. Although adduction and hydrogen bonding of solvent components account for solvent loss, other degradative reactions also account for loss of original solvent and solvent quality. Ring contraction of tetralin (9), and octahydrophenanthrene (8,10) under coal-liquefaction conditions reduces the hydrogen-donor concentration and therefore the solvent quality.

The use of a one-component solvent system can be misleading because reactions with coal may be occurring that normally would not occur if other components of a solvent were present. The objective of this study was to examine a multicomponent synthetic solvent and determine if solvent components are preferentially lost or degraded during short-contact-time liquefaction (SCTL), and how solvent loss in SCTL compares with other liquefaction conditions that involve gradual heat-up.

EXPERIMENTAL

Experiments were performed in a microreactor assembly (11) consisting of a 316 stainless steel 1/2-in. union tee with two end caps. Five grams of a synthetic solvent and one gram of moisture-free Western Kentucky 9/14 coal were added to the microreactor, which was assembled and pressurized to 1100 psig with H_2. The synthetic solvent consisted of 4% quinoline, 13% m-cresol, 20% tetralin, 33% 1-methylnaphthalene, 20% phenanthrene, and 10% pyrene. Experiments were conducted with one- and two-component solvents and coal in order to identify unique products from each of the simple solvent systems. The two-component solvent consisted of 20% pyrene and 80% tetralin, or 20% phenanthrene and 80% tetralin. One-component solvents of 1-methylnaphthalene, tetralin, and m-cresol were also used. The microreactor assembly was attached to a wrist-action shaker that moved the reactor through a small arc for adequate mixing of the reactor contents. The shaker was positioned above a vertically moving platform that supported a fluidized sand bath (11).

For SCTL experiments, the bath was heated to an initial temperature of 460°C. When the experiment was initiated, the temperature set point was changed to 425°C and the platform (with bath) was raised, immersing the microreactor. Heat-up to 425°C took approximately 1 min. Reaction time was 3 min at 425°C. For experiments conducted under traditional or severe conditions, the reactor was immersed in the sand bath, which was at room temperature, gradually heated (55 min) to 425°C, and held at reaction temperature for 30 min or 6 hours. At the end of the

reaction, the platform was lowered and the microreactor was cooled with a stream of room-temperature air. The outside of the cooled microreactor assembly was cleaned (to remove sand) with compressed air. Gases were vented, and the micro-reactor was disassembled.

The reacted suspension was pipetted into a 50-mL volumetric flask containing 0.100 gm durene and 0.100 gm fluorenone, which were the internal standards used for quantitative capillary gas chromatography. The remaining residue and synthetic solvent in the microreactor were removed with tetrahydrofuran (THF) and added to the flask. Aliquots were then analyzed using a 50-meter highly cross-linked phenylmethylsilicone capillary column. Flame ionization was used to detect individual components of the treated synthetic solvent, although in certain instances a mass-selective detector was also used to assist in the identification of products.

Solvent loss of each component was determined by calculating the difference between the original amount of the component and the recovered amount of the component and its reaction by-products. Solvent that was lost and unaccounted for represented adducted or polymerized material. All percentages will be discussed on an absolute basis; therefore, the loss of 10% tetralin would represent 10% of the synthetic solvent and not 10% of the 20% tetralin present in the synthetic solvent. The solvent losses would be five times larger if they were based on the weight of the coal sample, since the solvent:coal ratio was 5:1, i.e., loss of 3% of the solvent by adduction would represent a 15% addition to the weight of the coal.

RESULTS AND DISCUSSION

The effect of reaction conditions on solvent loss, and specifically on pref-erential loss of components of the solvent, was examined at three sets of reaction conditions. Experiments were conducted under SCTL conditions (rapid heat-up, 3 min at 425°C), traditional conditions (gradual heat-up, 30 min at 425°C), and severe conditions (gradual heat-up, 6 hours at 425°C). The advantages in using this synthetic solvent are that all components of the solvent are known, its elemental composition is similar to a coal-derived recycle solvent, and the multi-component solvent simulates a recycle solvent better than a one-component solvent does. The use of a synthetic solvent also allows the study of individual com-ponents in a more realistic environment.

The objective was to examine solvent recovery with increasing severity of coal-liquefaction reaction conditions. The SCTL stage of an ITSL process involves rapid heat-up, followed by a short residence time at reaction temperature. During rapid heat-up, the rate of free-radical production should increase significantly in a SCTL stage. An increase in free-radical concentration was hypothesized, since the demand for hydrogen, with increased free-radical production, would increase and would be less likely satisfied by hydrogen donors and gaseous hydrogen. With an increase in free-radical concentration, a concomitant increase in solvent adduction was hypothesized, since free-radical addition, aromatic sub-stitution, and polymerization reactions involving solvent and coal free-radicals would be likely.

In comparing results obtained under SCTL conditions (Table 1) with results obtained from experiments conducted under traditional liquefaction conditions (gradual heat-up to 425°C, 30 min at 425°C), solvent loss due to adduction should also be occurring under traditional conditions. As the severity of the lique-faction conditions is increased, adducted solvent should undergo cleavage (crack-ing, hydrogenolysis, etc.) and re-form solvent-like products, resulting in improved solvent balance. While the original components may not be recovered, products having similar structures and chemical properties should be. For example, adduction of phenanthrene with a coal-derived benzylic radical may occur

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and may ultimately form methyl-substituted phenanthrene (Figure 1). Based on this hypothesis, severe solvent loss was expected with a SCTL process compared to moderate solvent loss under traditional liquefaction conditions, and if the conditions were severe enough, solvent that was initially adducted, or solvent-like products, could be recovered.

Results from SCTL reactions demonstrated that components of the synthetic solvent were not adducted, degraded, or lost. While 75%-85% of the coal was converted to THF-soluble material, only 2.6% tetralin underwent dehydrogenation. No adduction of m-cresol or quinoline was observed. Results using a synthetic solvent demonstrate that SCTL is a favorable process because solvent balance with little solvent degradation can be achieved. These results were unexpected and suggest that an increased concentration of free radicals in a short period of time does not cause solvent loss or degradation when sufficient readily donable hydrogen is present. The results also imply that free radical production does not play an important role in solvent loss via adduction.

It should also be understood that little, if any, of the recovered, original solvent components are coal-derived. Based on coal experiments performed with one- and two-component solvents, negligible quantities of quinoline, m-cresol, and 1-methylnaphthalene could be considered coal-derived, while a maximum of 0.2% tetralin, 0.3% naphthalene, 0.2% pyrene, and 0.1% phenanthrene were coal-derived.

Experiments conducted using traditional coal liquefaction reaction conditions showed that solvent balance could still be achieved, but degradation of the solvent had started to occur. Results from experiments performed in the absence of coal showed that little, if any, demethylation and decomposition of 1-methylnaphthalene had occurred. Reactions in the presence of coal showed that approximately 3.2% 1-methylnaphthalene had undergone demethylation and decomposition. Some of the demethylated product (2.2%) could be accounted for by the increased amounts of naphthalene. Tetralin reactions included dehydrogenation to naphthalene (6.1%), rearrangement to 1-methylindane (0.5%), and decomposition to butylbenzene (0.1%). The total amount of tetralin and its reaction products is 22.2%; therefore, the additional amount (based on 20% tetralin in the synthetic solvent) could be accounted for by demethylation of 1-methylnaphthalene. It is possible that more than 2.2% 1-methylnaphthalene underwent demethylation to naphthalene if tetralin was being lost via unidentified reactions and not via dehydrogenation to naphthalene. If this occurred, then greater amounts of recovered naphthalene could be attributed to the demethylation of 1-methylnaphthalene and not to the dehydrogenation of tetralin. Methylation was also occurring, and 0.4% dimethylnaphthalene and 0.3% dimethylphenol were produced. Hydrogenation of the aromatic components was also occurring, producing 1.0% methyltetralin, 1.7% dihydrophenanthrene, 0.1% tetrahydrophenanthrene, 0.8% dihydropyrene, and 1.3% tetrahydroquinoline. The production of methyltetralin is most likely occurring via the hydrogenation of 1-methylnaphthalene, since no methylation of tetralin was observed when blank experiments using tetralin as a solvent were conducted. The major degradation reactions occurring were rearrangement of tetralin to 0.5% 1-methylindane (Equation 1) and cracking to butylbenzene (0.1%).

1)
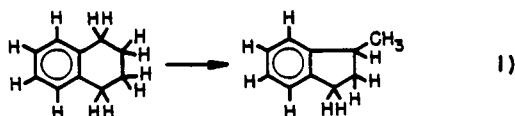
While some of the quinoline was undergoing hydrogenation to tetrahydroquinoline (1.3%), 0.3% could not be accounted for. Solvent balance under traditional lique-faction conditions was quite good. While methylation, demethylation, rearrange-ment, and cracking reactions have become apparent, 98.6% of the solvent can still be accounted for (less possible coal-derived products) and had not been lost because of adduction with coal-derived products.

Treatment of coal and solvent at more severe conditions resulted in greater rearrangement and degradation of the individual solvent components, although the solvent balance was approximately 97.5%. As much as 16.5% of 1-methylnaphthalene had undergone reaction. At least 12% 1-methylnaphthalene could be accounted for because of demethylation, methylation, and hydrogenation. Extensive dehydro-genation of tetralin was expected, and only 6.3% tetralin was recovered. Rearrangement reactions were significant and again were a major reason for the decrease in solvent quality. Approximately 2.1% tetralin had rearranged to 1-methylindane. Some loss of most components of the solvent had occurred. Methylation and demethylation of m-cresol was greater than observed under traditional liquefaction conditions, and approximately 11.1% was recovered. While quinoline represented the component that was present in the smallest amount, it was preferentially lost, and only 1.8% of quinoline and tetrahydroquinoline could be accounted for. While most of the solvent could be accounted for (approximately 97.5%), only 61.1% was recovered as original solvent and represented a solvent of much poorer quality.

Experiments conducted under these severe reaction conditions have shown that the synthetic solvent has undergone many reactions. Degradation reactions were evident; and greater, not lesser, quantities of solvent were lost. Even under these severe conditions, the overall solvent balance was better than expected.

SUMMARY

The effect of reaction conditions on solvent loss was determined. Solvent recovery and solvent balance were better than expected for SCTL and traditional liquefaction conditions. Surprisingly, very little adduction of solvent com-ponents was observed. Increased severity of reaction conditions caused an increase in degradation of the synthetic solvent and an increase in adduction (approximately 2.5%). From these results, the extent of solvent adduction under most liquefaction conditions is minimal, and the solvent quality is most affected because of increased degradation with increasing severity.

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TABLE 1. Solvent Recovery Values

| Components and Percentages in Original Synthetic Solvent		Percentage of Components in Reacted Synthetic Solvent[1]					
		Reaction Conditions					
		SCTL		Traditional		Severe	
		Solvent	Coal + Solvent	Solvent	Coal + Solvent	Solvent	Coal + Solvent
1-Methylnaphthalene	33	33.3	32.8	32.7	28.4	27.9	16.5
Dimethylnaphthalenes	--	--	--	--	0.4	1-	0.6
Methyltetralins	--	--	--	0.1	1.0	1.2	2.0
Tetralin	20	20.1	17.5	19.6	15.5	16.6	6.3
Naphthalene	--	0.1	2.6	0.4	6.1	3.8	20.4
Ethylbenzene	--	--	--	--	--	--	0.1
Methylindane	--	--	--	0.2	0.5	1.7	2.1
Butylbenzene	--	--	--	0.1	0.1	0.2	0.4
Phenanthrene	20	20.1	19.8	19.4	18.1	17.3	17.3
Dihydrophenanthrene	--	0.1	0.5	0.8	1.7	2.4	0.8
Tetrahydrophenanthrene	--	--	--	--	0.7	0.3	0.5
m-Cresol	13	12.9	12.7	12.7	12.1	11.7	11.1
Dimethylphenol	--	--	--	--	0.3	--	0.7
Phenol	--	--	--	--	0.1	0.1	0.3
Pyrene	10	9.8	9.6	9.2	8.5	8.3	8.4
Dihydropyrene	--	0.1	0.1	0.7	0.8	1.4	0.5
Quinoline	4	4.1	4.0	3.3	2.4	1.6	1.5
Tetrahydroquinoline	--	0.1	0.1	0.8	1.3	1.6	0.3
Unidentified Solvent-Derived Products	--	--	--	0.3	1.2	2.7	4.9
Unidentified Solvent-Derived and/or Coal-Derived Products	--	--	--	--	1.5	--	2.8
Total Recoveries		100.7	99.8	100.3	100.1	98.8	97.5

[1]Values represent average of at least duplicate experiments.
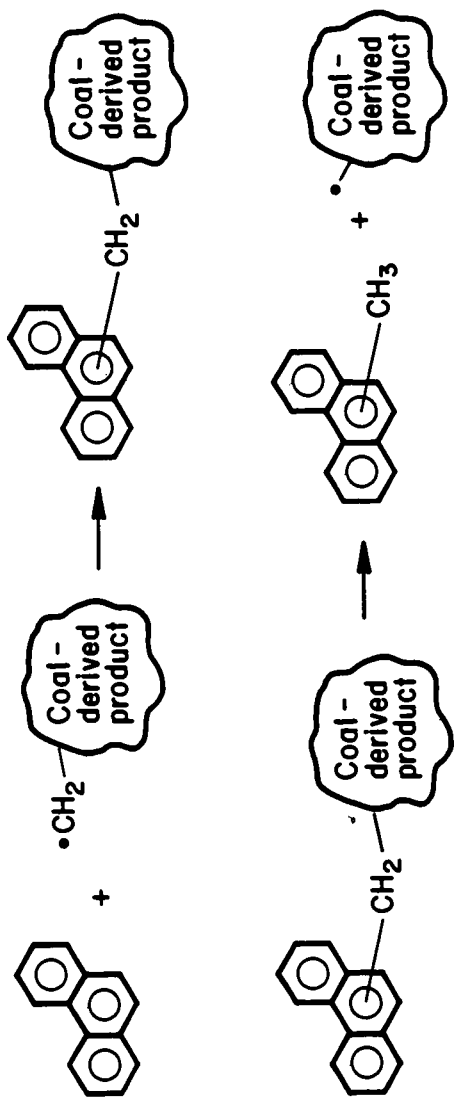
Figure 1. Methylation of Solvent by Coal